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Nitrate Biogeochemistry and Reactive Transport in California Groundwater: LDRD Final Report

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FY05 LDRD Final Report

Nitrate Biogeochemistry and Reactive Transport in California Groundwater

LDRD Project Tracking Code: 03-ERD-067

Bradley K. Esser, Principal Investigator

Introduction and Background

Nitrate contamination is a significant threat to groundwater in California and other states. Successful groundwater management requires science-based simulation of future impacts in affected aquifers and science-based assessment of management practices designed to reduce nitrate levels. An important component of developing science-based approaches is the need to develop new and better tools for the characterization and quantification of biogeochemical reactions in the subsurface that control the fate and transport of nitrate in groundwater. When coupled with our ability to characterize groundwater flow and to model reactive transport, these new tools will allow an accurate assessment of the future distribution of nitrate in California aquifers and of the impact of different management practices on nitrate input to groundwater. Such assessment is vital to making cost-effective management and policy decisions regarding land use and groundwater remediation.

Research Activities

Our research investigated the fate and transport of nitrate in groundwater at two scales, with an emphasis on microbial denitrification :

- *Field scale*: denitrification in the shallow saturated zone at a dairy farm in the Central Valley, and
- *Basin scale*: nitrate transport in two impacted basins.

The research focused on developing and applying rapid methods to quantify denitrification in order to assess the role of denitrification in the shallow and deep saturated zone, and to allow quantitative assessment of the kinetics of microbially-mediated denitrification in groundwater systems.

The research supported a number of students, including two LLNL postdocs.

- Tracy LeTain, SEP, LLNL postdoc (Harry Beller, advisor)
- Michael Singleton, CMS Directorate Postdoc (Bradley K. Esser advisor)

- Keara Moore, University of Arizona (Brenda Ekwurzel, advisor): Keara's work on nitrate source attribution and transport in the Livermore-Amador Basin formed the core of her M.S. thesis.
- Brad Cey, University of Texas at Austin (Bridget Scanlon, advisor): Brad is using the dairy site that was developed with LDRD funding in his doctoral research.
- Glenn Shaw, UC-Merced (Martha Conklin, advisor): Glenn participated in sampling at the dairy site, and spent a summer working at the lab.

Technical accomplishments

- We developed a quantitative polymerase chain reaction method for functional nitrite reductase genes to assay denitrifier populations in soil and in water;
- We determined denitrification rate constants for an autotroph with Fe monosulfide;
- We installed several multilevel wells and performed a synoptic water and soil survey at a Central Valley dairy that allowed us to demonstrate localized denitrification in stratified groundwater;
- We used real-time qPCR to determine denitrifier populations in soil cores taken from the dairy wells, and demonstrated that denitrification was strongly localized at the oxic-anoxic interface at this site;
- We developed a new tracer for manure lagoon seepage that allows us to distinguish wastewater recharge through lagoon seepage from wastewater recharge through field application of wastewater.
- We developed geochemical models of manure lagoon seepage impacts on dairy groundwater
- We analyzed groundwater in the Llagas and Livermore-Amador Basins for age, recharge temperature, and excess nitrogen;
- We developed a structural model and a geostatistical model for basin permeability in the Llagas Basin, and used this model to assess aquifer vulnerability.
- We used groundwater age dating, excess nitrogen, and nitrate isotopic composition along with traditional approaches to determine the source of high groundwater nitrate in the Livermore-Amador Basin
- We used geochemical models with public water-quality data to show that high nitrate levels are associated with fertilization;

Exit Plan

The exit plan assumed that a better understanding of nitrate fate and transport in groundwater would allow development of a robust approach to assessing past impacts and predicting future impacts of different management plans and land use patterns on local groundwaters. Our primary target for follow-on sponsorship was the California EPA State Water Resources Control Board (SWRCB), and we were successful. The SWRCB currently funds LLNL through the GAMA program to assess State groundwater

vulnerability (~\$1.2M/year), and now has a legislative mandate and a \$50M allocation from Proposition 50 to comprehensively assess groundwater basin water quality. In 2003, James Giannopoulos, head of SWRCB Clean Water Programs, wrote a letter to LLNL encouraging investigation of the impact of high nitrate in groundwater and offering SWRCB's support and collaboration. In the most recent contract, the largest single special studies task (\$600K) was for assessment of nitrate contamination at California dairies. Two other tasks focused on nitrate co-contaminants (including both characterization of groundwater to distinguish nitrate sources and development of methods for commercialization) and an additional task focused on documenting the presence or absence of denitrification in California drinking water aquifers. All told, follow-on funding has been in excess of \$1M. More importantly, LLNL now has a lead role in heading up special studies for the GAMA program, which will continue for at least five more years.

We have also been successful in obtaining funding to examine the impact of management practices on nitrate loading at California dairies. As co-PIs with Sustainable Conservation, a non-profit group based in California, we developed a \$2M proposal entitled "*Reducing Water Quality Impacts from Dairies in the San Joaquin and Tulare Lake Drainage Basins*" that was submitted to the State of California Dairy Water Quality Grant Program (funded through Proposition 50). This January, we learned that the proposal was successful, and \$250K will come to LLNL.

The project also allowed us to develop academic collaborations. The project supported a Master's student from the University of Arizona, and a doctoral student from the University of Texas at Austin. Walt McNab was invited to present results from this project at the UC-Davis Hydrology Departments Distinguished Lecturer Series. We will be collaborating with Thomas Harter, of UC-Davis and the UC Cooperative Extension, on a CalFed-funded project to monitor Central Valley Dairies. This will give us credibility with CalFed, and enable us to apply to future CalFed Proposition 50 calls. We are developing mechanisms to work with Roger Bales and Martha Conklin at UC-Merced, and sponsored their first UC-Merced graduate student last summer. We will also provide support to UC-Davis in their NSF Proposal to become a Center of Excellence. If successful, this will give LLNL ready access to graduate students.

We have briefed a number of agencies and stakeholders on this project, including the State Water Resources Control Board, and national-level EPA regulatory (Office of Water) and research (NERL) branches. We have also presented the project to the IAEA Isotope Hydrology program at an invitation-only technical workshop. Below are briefings that are not included in the Presentations and Publications section that follows.

Briefings

Esser B. K. (2004) Nitrate biogeochemistry and reactive transport in California groundwater (abstr.). *CMS Directorate Review Committee (LLNL, November 9, 2004)*.

Esser B. K. (2004) Nitrate biogeochemistry and reactive transport in California groundwater (abstr.). In *CMS Directorate Review Committee*

- Esser B. K. (2005) Water Resources Research at LLNL: Nitrate transport & denitrification in groundwater at a Central Valley dairy farm (abstr.). *USDA/NRCS Kings County Field Office (Hanford, December 13, 2005)*.
- Esser B. K., Moran J., Hudson G. B., and Singleton M. (2005) Denitrification in groundwater underlying a Kings County dairy operation (abstr.). *State Water Resources Control Board, Clean Water Office (Sacramento, May 27, 2005)*.
- Esser B. K., Moran J., and Singleton M. (2005) Denitrification in groundwater underlying a Kings County dairy operation (abstr.). *Sustainable Conservation (LLNL, August 23, 2005)*.
- Esser B. K., Moran J., and Singleton M. (2005) Denitrification in groundwater underlying two Central Valley dairy operations (abstr.). *U. S. Environmental Protection Agency, Region 9 Groundwater Office (San Francisco, June 21, 2005)*.
- Esser B. K. and Moran J. E. (2005) California dairy and groundwater research at LLNL. *California State Assembly staffers (Gail Delihant, Doug Haaland) (LLNL, October 5, 2005)*.
- Esser B. K. and Moran J. E. (2005) Water use management & groundwater age dating at LLNL. *U. S. Bureau of Reclamation staff (LLNL, November 29, 2005)*.
- Esser B. K., Moran J. E., and Singleton M. (2005) Nitrate transport & denitrification in groundwater: New approaches to characterization and modeling. *Western United Dairymen (LLNL, May 10, 2005)*.
- Leif R., Beller H. R., Moody-Bartel C., and Esser B. K. (2004) Organic co-contaminants in a nitrate-contaminated aquifer (abstr.). *Barbara Smith, USEPA Region 9 (LLNL, August 23, 2004)*.

Presentations and Publications

Invited presentations

- Carle S. F., Esser B. K., Hudson B., Moran J. E., McNab W., and Beller H. R. (2004) Perched canal-recharge aquifers: A sustainable agricultural water supply given nitrate loading? (abstr.). *13th Annual GRA Meeting and Conference: Managing Aquifers for Sustainability, Protection, Restoration, Replenishment and Water Reuse (Rohnert Park, September 23-24, 2004)*. (UCRL-ABS-203837) (Conference talk, invited)
- Carle S. F., Tompson A. F. B., and Esser B. K. (2004) Modeling basin-scale nitrate transport considering alluvial and biogeochemical heterogeneity (abstr.). *Geological Society of America Annual Meeting (Denver; November 7-10, 2004)*. (UCRL-ABS-208496) (Conference talk, invited)
- Esser B. K. (2003) The use of isotopic techniques to assess contaminant loading and transport in California groundwater, with an emphasis on nitrate (abstr.). *IAEA Isotope Hydrology Technical Meeting "Assessing the Use of Isotopic Techniques for Evaluating Impacts of Irrigation Practices on Groundwater Quality and Quantity" (Vienna; November 17-20, 2003)*. (Workshop, invited)
- Esser B. K. (2004) Nitrate in California groundwater: Sources, sinks and transport (abstr.). *Groundwater Resources Association of California, San Francisco Branch Meeting (Oakland; October 20, 2004)*. (Seminar, invited)
- McNab W. (2004) Nitrate in California groundwater: An overview of source loading and denitrification on different spatial scales (abstr.). *California Water and Environmental Modeling Forum 2004 Annual Meeting: Ten Years of Promoting Excellence and Consensus in Water and Environmental Modeling (Pacific Grove; February 24-26, 2004)*. (Conference, invited talk)
- McNab W. (2004) Nitrate in California groundwater: Mass loading and reactive transport across different spatial scales (abstr.). *UC-Davis Distinguished Speaker Series, Department of Civil and Environmental Engineering (Davis, February 19, 2004)*. (Seminar, invited)
- McNab W. (2004) Session Eighteen: Integrating State-Wide Groundwater Data Sets to Assess Anthropogenic Impacts to California Groundwater (session). *California Water and Environmental Modeling Forum 2004 Annual Meeting: Ten Years of Promoting Excellence and Consensus in Water and Environmental Modeling (Pacific Grove, February 24-26, 2004)*. (Conference session chair, invited)

Moran J. E. and . (2004) Concurrent Session 3B: Groundwater Contaminants Today and Tomorrow. *13th Annual Groundwater Resources Association of California Meeting and Conference: Managing Aquifers for Sustainability, Protection, Restoration, Replenishment and Water Reuse (Rohnert Park, September 23-24, 2004)*. (Conference session chair, invited)

Conference/Meeting Abstracts

- Carle S. F., Esser B. K., McNab W. W., Moran J. E., and Singleton M. J. (2005) Simulation of canal recharge, pumping, and irrigation in a heterogeneous perched aquifer: Effects on nitrate transport and denitrification (abstr.). *25th Biennial Groundwater Conference and 14th Annual Meeting of the Groundwater Resources Association of California (Sacramento, CA; October 25-26, 2005)*. (UCRL-POST-217056) (Conference poster)
- Carle S. F., Tompson A. F. B., McNab W. W., Esser B. K., Hudson G. B., Moran J. E., Beller H. R., and Kane S. R. (2004) Simulation of nitrate biogeochemistry and reactive transport in a California groundwater basin. *Computational Methods in Water Resources International Conference XIV (Chapel Hill, June 13-17, 2004)*, 12 pp. (UCRL-CONF-201876, UCRL-ABS-201851) (Conference proceedings, invited, peer-reviewed article)
- Esser B. K., Beller H. R., Carle S. F., Hudson G. B., Kane S. R., LeTain T. E., McNab W. W., and Moran J. E. (2005) New approaches to characterizing microbial denitrification in the saturated zone (abstr.). *Geochimica et Cosmochimica Acta* 69(10), A229. 15th Annual Goldschmidt Conference (Moscow, ID, May 20-25, 2005). (UCRL-ABS-209086-DRAFT) (Conference poster)
- Esser B. K., Beller H. R., Carle S. F., Hudson G. B., Kane S. R., LeTain T. E., McNab W. W., Moran J. E., and Singleton M. J. (2005) Characterization of saturated-zone denitrification in a heterogeneous aquifer underlying a California dairy (abstr.). *25th Biennial Groundwater Conference and 14th Annual Meeting of the Groundwater Resources Association of California (Sacramento, CA; October 25-26, 2005)*. (UCRL-POST-216853) (Conference poster)
- Esser B. K., Beller H. R., Carle S. F., Hudson G. B., Kane S. R., McNab W. W., Moran J. E., and Tompson A. F. B. (2004) Denitrification in a shallow aquifer underlying a dairy farm in the Central Valley of California (abstr.). *Eos, Transactions, American Geophysical Union* 85(47), Abstract H43B-0373. 2005 AGU Fall Meeting (San Francisco, December 13-17, 2004). (UCRL-ABS-206433) (Conference poster)
- Esser B. K., Carle S. F., Hudson G. B., Leif R., Letain T., Moran J. E., McNab W., and Tompson A. F. B. (2004) Denitrification in a shallow aquifer underlying a dairy farm: New approaches to characterization and modeling (abstr.). *13th Annual Groundwater Resources Association of California Meeting and Conference: Managing Aquifers for Sustainability, Protection, Restoration, Replenishment and Water Reuse (Rohnert Park, September 23-24, 2004)*. (UCRL-PRES-207404) (Conference talk)
- Esser B. K., Hudson G. B., Moran J. E., Carle S. F., McNab W. W., Tompson A. F. B., Moore K., Beller H. R., and Kane S. R. (2003) Reactive transport of nitrate in northern California groundwater basins: An integrated characterization and modeling approach (abstr.). *Groundwater Resources Association of California 24th Biennial Groundwater Conference and 12th Annual Meeting (Ontario, CA; October 28-29, 2003)*, Poster presentation. (Conference poster)
- Esser B. K., Letain T. E., Singleton M. J., Beller H. R., Kane S. R., Balser L. M., and Moran J. E. (2005) Molecular and geochemical evidence of *in-situ* denitrification at a dairy field site in the Central Valley of California (abstr.). *Eos, Transactions, American Geophysical Union* 86(52), Abstract B31A-0972. 2005 AGU Fall Meeting (San Francisco, December 5-9, 2005). (Conference poster)
- Esser B. K., Moran J., Hudson G. B., Carle S. F., McNab W. W., Tompson A. F. B., Moore K., Beller H. R., Kane S. R., and Eaton G. F. (2003) Reactive transport of nitrate in northern California groundwater basins: An integrated characterization and modeling approach (abstr.). *Eos, Transactions, American Geophysical Union* 84(46), Abstract H52C-07. 2003 AGU Fall Meeting (San Francisco, December 12, 2005). (UCRL-ABS-208862) (Conference talk)
- Hudson G. B., Beller H. R., Esser B. K., Grayson A. R., Hu Q., Kane S. R., Leif R. N., Moran J. E., and Moody-Bartel C. (2004) Emerging contaminants in water resources: Status, challenges, and a

- case study (abstr.). *2nd International Conference on Soil Pollution and Remediation (Nanjing, China; November 9-12, 2004)*. (UCRL-ABS-206964) (Conference talk)
- McNab W., Moran J. E., and Esser B. K. (2004) Geochemical signatures of fertilizers and soil amendments in public water supply aquifers in California (abstr.). *13th Annual GRA Meeting and Conference: Managing Aquifers for Sustainability, Protection, Restoration, Replenishment and Water Reuse (Rohnert Park, September 23-24, 2004)*. (UCRL-ABS-203860, UCRL-PRES-206327) (Conference talk)
- McNab W. W., Singleton M. J., Esser B. K., Moran J. E., Beller H. R., Kane S. R., LeTain T. E., and Carle S. F. (2005) Geochemical modeling of nitrate loading and denitrification at an instrumented dairy site in California's Central Valley (abstr.). *25th Biennial Groundwater Conference and 14th Annual Meeting of the Groundwater Resources Association of California (Sacramento, October 25-26, 2005)*. (UCRL-POST-216428) (Conference poster)
- McNab W. W., Jr., Singleton M. J., Esser B. K., Moran J. E., Beller H. R., Kane S. R., Letain T. E., and Carle S. F. (2005) Nitrate loading and groundwater chemistry at a dairy site in California's Central Valley (abstr.). *International Conference on Safe Water 2005 (San Diego, October 21-25, 2005)*. (Conference talk)
- Moran J. E., Esser B. K., Hudson G. B., Singleton M., McNab W. W., Carle S. F., Beller H. R., Leif R., and Moody-Bartel C. (2005) The effects of agricultural nitrate sources on groundwater supplies in California (abstr.). *Geological Society of America Annual Meeting (Salt Lake City, October 15-19, 2005)*. (UCRL-ABS-213498) (Conference talk)
- Moran J. E., Leif R., Esser B. K., and Singleton M. J. (2006) Evidence for groundwater contamination vulnerability in California's Central Valley (abstr.). *2006 California Plant and Soil Conference (Visalia, February 7-8, 2006)*. (UCRL-PROC-217713) (Conference talk)
- Moran J. E., Moore K., McNab W., Esser B. K., Hudson B., and Ekwurzel B. (2005) Sources and transport of nitrate in the Livermore Valley Groundwater Basin (abstr.). *Joint GSA-AAPG Cordilleran Section Meeting (San Jose, April 29 - May 1, 2005)*. (Conference talk)
- Singleton M. J., Esser B. K., Moran J. E., McNab W. W., and Leif R. N. (2005) Natural tracers of lagoon seepage at California dairies (abstr.). *25th Biennial Groundwater Conference and 14th Annual Meeting of the Groundwater Resources Association of California (Sacramento, October 25-26, 2005)*. (UCRL-ABS-214160; UCRL-POST-216845) (Conference poster)
- Singleton M. J., Hudson G. B., Beller H. R., Esser B. K., Moran J. E., Kane S. R., Carle S., Tompson A., Letain T. E., Legler T. C., and Balser L. M. (2005) Viability of intrinsic denitrification to reduce nitrate pollution at California dairies (abstr.). *American Chemical Society National Meeting (Washington, DC; August 28 - September 1, 2005)*. (UCRL-ABS-212107) (Conference talk)
- Singleton M. J., Moran J. E., Esser B. K., Leif R. N., McNab W. W., Carle S. F., and Moore K. B. (2005) Evaluation of nitrate sources and nitrate management strategies in California suburban growth areas (abstr.). *Eos, Transactions, American Geophysical Union* 89(52), Abstract B43C-0295. 2005 AGU Fall Meeting (San Francisco, December 5-9, 2005). (Conference poster)

Refereed publications

- Carle S. F., Esser B. K., and Moran J. E. (2006) High-resolution simulation of basin scale nitrate transport considering aquifer system heterogeneity. *Geosphere* (Special Issue: Modeling Flow and Transport in Physically and Chemically Heterogeneous Media), (In Press). (UCRL-JRNL-214721) (Journal article, invited)
- Carle S. F., Tompson A. F. B., McNab W. W., Esser B. K., Hudson G. B., Moran J. E., Beller H. R., and Kane S. R. (2004) Simulation of nitrate biogeochemistry and reactive transport in a California groundwater basin. *Computational Methods in Water Resources International Conference XIV (Chapel Hill, June 13-17, 2004)*, 12 pp. (UCRL-CONF-201876, UCRL-ABS-201851) (Journal article, invited)
- Moore K., Ekwurzel B., Esser B. K., Hudson G. B., and Moran J. E. (2006) Nitrate source history for Livermore, California using environmental isotopes, noble gases and major ions. *Applied Geochemistry*, (In Press). (UCRL-JRNL-207110) (Journal article)

Technical Reports

- Moran J. E., Beller H., Eaton G. F., Ekwurzel B. E., Esser B. K., Hu Q., Hudson G. B., Leif R., McNab W., and Moody-Bartel C. (2005) California GAMA program: Sources and transport of nitrate in groundwater in the Livermore Valley Basin, California, pp. 30. Lawrence Livermore National Laboratory. (UCRL-TR-217189) (Report)
- Moran J. E., McNab W. W., Esser B. E., and Hudson G. B. (2005) California GAMA program: Sources and transport of nitrate in shallow groundwater in the Llagas Basin of Santa Clara County, California, pp. 37. Lawrence Livermore National Laboratory. (UCRL-TR-213705) (Report)

Manuscripts submitted

- Singleton M. J., Esser B. K., Moran J. E., McNab W. W., and Harter T. (2006) Saturated zone denitrification: potential for natural attenuation of nitrate contamination in shallow groundwater under dairy operations. *Environmental Science & Technology*. Submitted. (UCRL-JRNL-219422-DRAFT) (Journal manuscript)
- McNab W. W., Jr., Singleton M. J., Moran J. E., and Esser B. K. (2006) Assessing the impact of animal waste lagoon leachate on the geochemistry of an underlying shallow aquifer. *Applied Geochemistry*. Submitted. (UCRL-JRNL-219615) (Journal manuscript)

Manuscripts in preparation

- Esser B. K., Beller H. R., Carle S. F., Hudson G. B., Kane S. R., LeTain T. E., McNab W. W., and Moran J. E. (2006) New approaches to characterizing microbial denitrification in the saturated zone. *Geobiology* (Special Issue: Geochemical Controls on Microbial Processes), *In preparation*. (Journal manuscript, invited)
- McNab W., Moran J. E., and Esser B. K. (2006) Geochemical trends associated with nitrate loading in groundwater in California: signatures of agricultural impacts to public water supply aquifers. (In preparation). (Journal manuscript)
- Moran J. E., Esser B. K., Beller H. R., Carle S. F., Hudson G. B., Kane S. R., McNab W. W., and Thompson A. F. B. (2006) Sources and transport of nitrate in shallow groundwater in the Llagas Subbasin of Santa Clara County, California. *In preparation*. (Journal manuscript)

LDRD Final Report Attachments

Six documents are attached. The first attachment is a 12-page peer-reviewed conference proceedings paper. Attachments 2 and 3 are manuscripts that have been accepted for publication in peer-reviewed journals. Note that attachments 1 and 2 are invited submissions. Attachments 4 and 5 are technical reports to the State Water Resources Control Board (SWRCB). They report research that was funded by this LDRD (03-ERD-067) and additional follow-on research that was funded directly by the SWRCB. As such they are evidence of a successfully implemented exit plan. In addition, attachment 5 is the basis of a manuscript being prepared for submission to a peer-reviewed journal. The final document (Attachment 6) is a Science Technology & Review article describing the LLNL Water Initiative, which includes this LDRD. Each document has been through review and release and has a UCRL number.

Attachment 1: Carle S. F., Tompson A. F. B., McNab W. W., Esser B. K., Hudson G. B., Moran J. E., Beller H. R., and Kane S. R. (2004) Simulation of nitrate biogeochemistry and reactive transport in a California groundwater basin. *Computational Methods in Water Resources International Conference XIV (Chapel Hill, June 13-17, 2004)*, 12 pp. (UCRL-CONF-201876, UCRL-ABS-201851)

Attachment 2: Carle S. F., Esser B. K., and Moran J. E. (2006) High-resolution simulation of basin scale nitrate transport considering aquifer system heterogeneity. *Geosphere* (Special Issue: Modeling Flow and Transport in Physically and Chemically Heterogeneous Media), (In Press). (UCRL-JRNL-214721)

Attachment 3: Moore K., Ekwurzel B., Esser B. K., Hudson G. B., and Moran J. E. (2006) Nitrate source history for Livermore, California using environmental isotopes, noble gases and major ions. *Applied Geochemistry*, (In Press). (UCRL-JRNL-207110)

Attachment 4: Moran J. E., McNab W. W., Esser B. E., and Hudson G. B. (2005) California GAMA program: Sources and transport of nitrate in shallow groundwater in the Llagas Basin of Santa Clara County, California, pp. 37. Lawrence Livermore National Laboratory. (UCRL-TR-213705)

Attachment 5: Moran J. E., Beller H., Eaton G. F., Ekwurzel B. E., Esser B. K., Hu Q., Hudson G. B., Leif R., McNab W., and Moody-Bartel C. (2005) California GAMA program: Sources and transport of nitrate in groundwater in the Livermore Valley Basin, California, pp. 30. Lawrence Livermore National Laboratory. (UCRL-TR-217189)

Attachment 6: Heller A., Newmark R., Duffy P., Esser B. K., and Bourcier B. (2004) Helping water managers ensure clean and reliable supplies. *Science & Technology Review* July/August 2004, p 4-13. (UCRL- TR-205144)



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Simulation of Nitrate Biogeochemistry and Reactive Transport in a California Groundwater Basin

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Nitrate is the number one drinking water contaminant in the United States. It is pervasive in surface and groundwater systems, and its principal anthropogenic sources have increased dramatically in the last 50 years. In California alone, one third of the public drinking-water wells has been lost since 1988 and nitrate contamination is the most common reason for abandonment. Effective nitrate management in groundwater is complicated by uncertainties related to multiple point and non-point sources, hydrogeologic complexity, geochemical reactivity, and quantification of denitrification processes. In this paper, we review an integrated experimental and simulation-based framework being developed to study the fate of nitrate in a 25 km-long groundwater subbasin south of San Jose, California, a historically agricultural area now undergoing rapid urbanization with increasing demands for groundwater. The modeling approach is driven by a need to integrate new and archival data that support the hypothesis that nitrate fate and transport at the basin scale is intricately related to hydrostratigraphic complexity, variability of flow paths and groundwater residence times, microbial activity, and multiple geochemical reaction mechanisms. This study synthesizes these disparate and multi-scale data into a three-dimensional and highly resolved reactive transport modeling framework.

1. BACKGROUND

Nitrate contamination is pervasive in surface and groundwater systems and is a growing problem in California. Greater than 40 percent of the State's population uses groundwater for at least a portion of their domestic needs, and some cities, such as Fresno, Davis, and

*This work was conducted under the auspices of the US Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract W-7405-Eng-48.

Lodi in the Central Valley, rely solely on groundwater. Since 1984, roughly 8,600 out of 25,000 wells in the State have been shut down, primarily because of nitrate contamination. About 10 percent of the currently operating public wells produce water that exceeds the regulatory drinking water standard (10 mg/L as N), and a much larger fraction produce water approaching this standard. As the population increases over the next 20 years, the loss of groundwater resources due to nitrate contamination will become an increasingly severe water supply issue [1]. Nitrate issues also affect the planned use of groundwater basins to store water in lieu of above-ground reservoirs [2].

Nitrate contamination is commonly viewed as intractable because it is ubiquitous, has multiple sources, and is expensive to treat. Contamination of groundwater is particularly problematic because aquifers have long response times (years to decades), and are heterogeneous and difficult to characterize. In California, the main anthropogenic activities that contribute nitrate to groundwater – fertilizers, confined animal feeding operations, and septic systems – are a legacy of commerce and growth over the last half-century, yet remain vital to the economic future of the State. Notably, the actual economic impacts of contamination, including the need to blend or treat water supplies, abandon wells, or secure alternative sources, are not well documented or understood.

Management of nitrate contamination requires quantitative assessments of (1) the source, distribution, and evolution of nitrate concentrations in affected aquifers, (2) the economic dimensions of the problem to implement cost-effective remediation, and (3) impact of land and water management practices that have been designed to reduce nitrate loading in order to implement effective source mitigation. All three goals require a fundamental understanding of fixed nitrogen transport and chemistry in the saturated zone on a basin scale.

The biogeochemical cycling of nitrogen between source areas near the ground surface and the vadose and saturated zones is complex and can be microbially mediated [3–6]. In oxic groundwater regimes, nitrate is anionic with no appreciable sorption. Microbial denitrification in the saturated zone facilitates the conversion of nitrate to dissolved molecular nitrogen (N_2), and is the ultimate sink for nitrate under low oxygen conditions. Characterizing the microbial controls and the kinetics of denitrification is essential to developing accurate reactive transport models for nitrate in groundwater. Developing such models also requires the ability to accurately characterize and model groundwater flow paths in heterogeneous media at both the field scale and basin scale.

2. THE LLAGAS SUBBASIN

This paper reviews the initial development of a basin-wide groundwater flow and transport model to study migration and fate of nitrate in the Llagas groundwater subbasin, situated in a narrow inland valley approximately 20 km south of San Jose, California (Fig. 1). Nitrate contamination of shallow groundwater is pervasive in many parts of the subbasin as a result of numerous rural and agricultural land uses [8,9]. Over the past

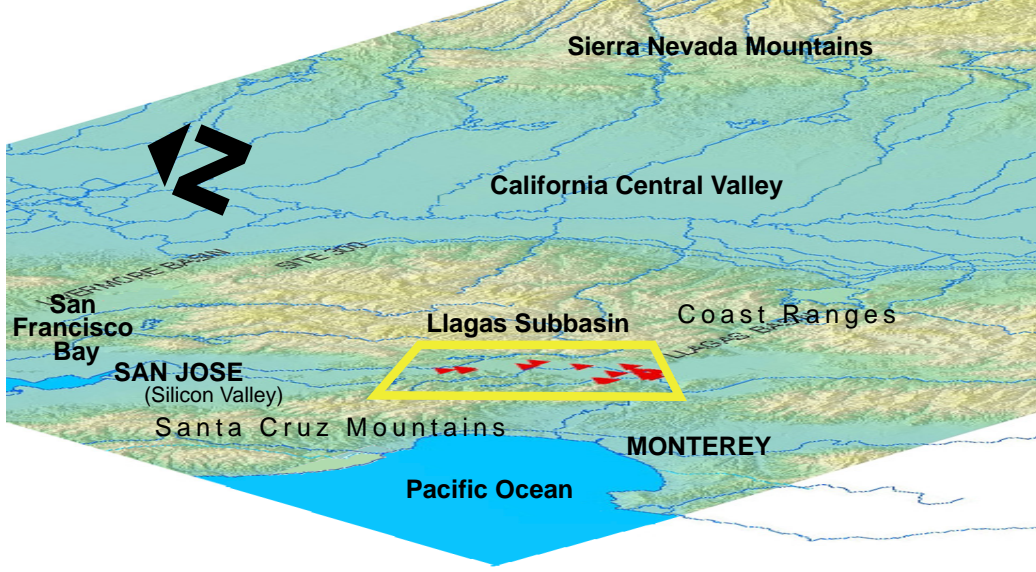


Figure 1. Bird's eye view of the Llagas subbasin location south of San Jose, California, looking northeastward.

50 years, these valley areas have undergone significant growth and urbanization due to their proximity to Silicon Valley, and groundwater provides the only source of water to some areas in the subbasin. The shallow zones are also threatened by widespread perchlorate contamination. Contamination in the shallow zones threatens deeper zones where increased water production is expected in the future to meet the demands of an increasing local population.

At its northern end, the subbasin extends from a groundwater divide (at its junction with the Coyote subbasin) to the south where it is bounded by the Pajaro River [7]. The subbasin is approximately 25 km long and ranges between 5 and 8 km wide. Annual precipitation ranges from less than 40 cm in the south to more than 60 cm in the north. Water level elevations (Fig. 2) indicate a southeasterly groundwater flow direction with significant natural recharge occurring where streams discharge into the subbasin south and northeast of Morgan Hill and west of Gilroy [10].

3. MODELING STRATEGY AND FRAMEWORK

Our reactive transport modeling approach focuses on the development of a hierarchical simulation framework that can be used as a means to assess the impacts of spatially variable nitrate loading, nitrate transport, and reactive (denitrification) processes between the water table and both shallow and deeper groundwater zones. Our simulation strategy

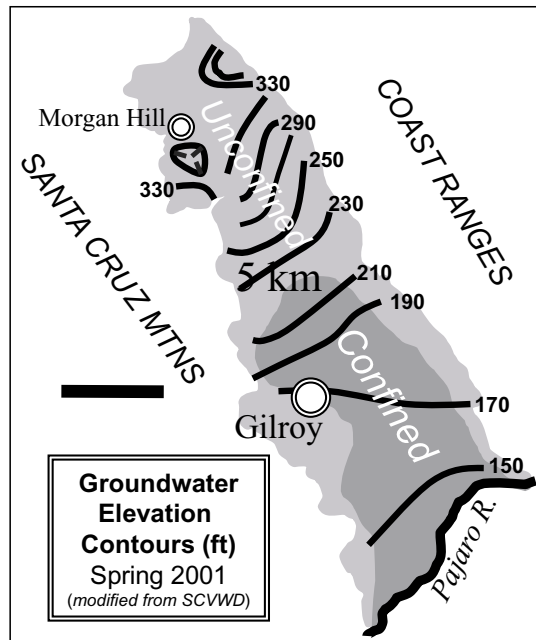


Figure 2. Map of Llagas subbasin showing groundwater elevation contours (in feet above sea level) for Spring, 2001. Modified from [10].

will be iterative and grounded, initially, in the development of a detailed geologic model. As discussed further below, flow model development will be guided by isotopic age dating measurements, noble gas tracer measurements, inverse geochemical models, and additional biogeochemical characterization of denitrification processes, as determined from both the field and laboratory. Ultimately, model simulations will allow the evaluation of important sensitivities and factors that control the flux, distribution, and residence times of nitrate in the subbasin and, thus, may form a basis for improving basin nitrate management strategies in the future.

3.1. Geostatistical Simulation of Hydrostratigraphy

The water bearing formations of the Llagas subbasin include Pliocene to Holocene age deposits of unconsolidated to semi-consolidated gravel, sand, silt and clay [7]. These include the deeper Santa Clara Formation and alluvial and alluvial fan deposits, which constitute the principal water producing zones. This and previous hydrogeologic interpretations [7,11] depict the hydrostratigraphic architecture as consisting of thick, gently dipping, and laterally continuous layers composed of three principle hydrofacies: (1) coarse-grained materials, (2) fine-grained materials including lacustrine deposits, and (3) alternating thin and discontinuous layers gravel and silt or clay. In a hydrogeologic context, these three hydrofacies can be regarded as aquifers, aquitards, and aquicludes, respectively.

Geostatistical simulation methods can be used to generate representative three-dimensional “realizations” of alluvial hydrofacies architecture [12–14]. In this study, realizations are designed to replicate the patterns of heterogeneity evident in the Llagas subbasin aquifer system. These patterns are deduced from geologic cross sections [7,11] and direct measurement of vertical transition probabilities from high-quality lithologic logs. Spatial variability of hydrofacies is quantified through a transition probability Markov approach [12–14]. The realizations are conditioned by lithologic logs, including driller’s logs, and can be adjusted to reflect larger scale structural patterns or trends such as dips or transitions between formations, e.g., [16].

The richest source of data that describe hydrofacies architecture is found in drillers’ logs, which, understandably, can be of variable quality. Over 300 drillers logs (Fig. 3) have been used to condition the geostatistical realizations developed in this study (Fig. 4). The size of the domain in this representation is 24 km (x) \times 8 km (y) \times 0.3 km (z). The spatial resolution is 100 m in the horizontal directions (x, y) and 2 m in the vertical (z), yielding over 2.8 million blocks in the model realization. Conditioning of the geostatistical realizations to drillers’ logs data is accomplished through a novel technique that accounts for data inaccuracy through assigned correlations between the data and true lithology [15]. For example, if a particular driller’s log is assumed absolutely correct in describing lithology, the assigned correlation is 1.0. Likewise, if the driller’s logs is assumed completely inaccurate, or “random”, the assigned correlation is 0.0.

The geostatistical simulation algorithm attempts to preserve spatial correlation inferred

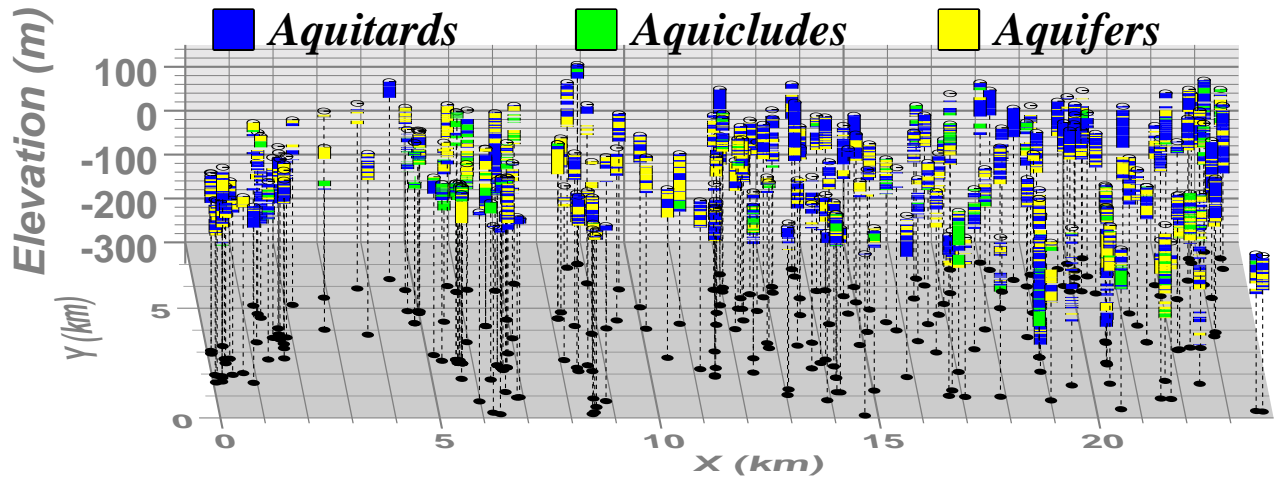


Figure 3. Driller's log lithologic data categorized as aquifers, aquitards, and aquicludes in Llagas subbasin (looking northeastward).

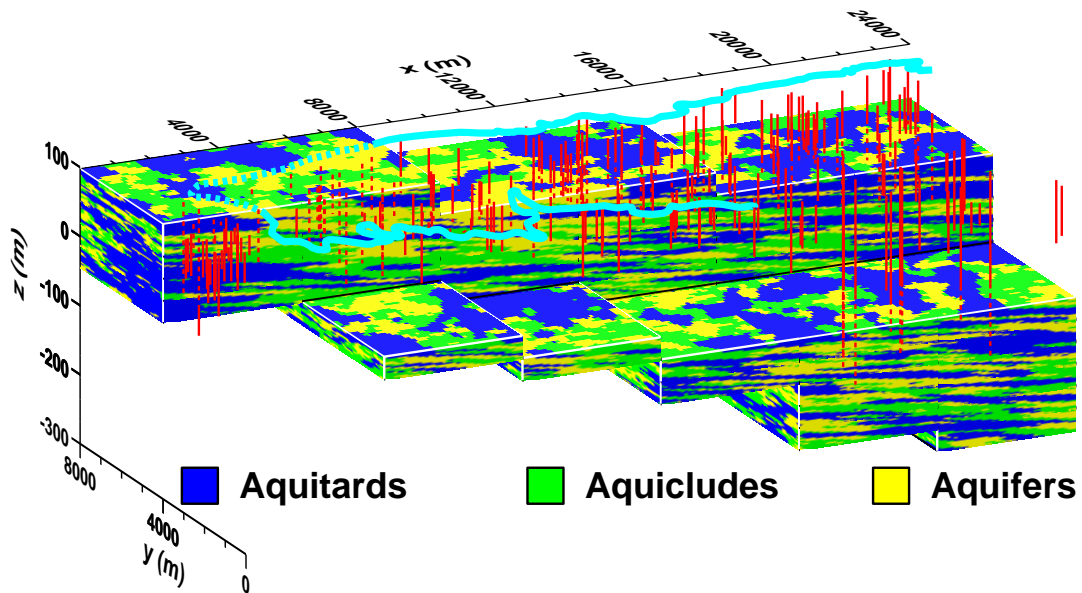


Figure 4. Example geostatistical realization of hydrofacies architecture in the Llagas subbasin, looking northeastward. The domain is 24 km long, 8 km wide, and 0.3 km deep, with a spatial resolution of 100 m in the horizontal directions and 1 m in the vertical. Red lines represent wells in Fig. 3. Light blue outline represents the subbasin boundary at the surface.

from the hydrofacies data; thus drillers' log data are honored to varying degrees depending on data quality. In this manner, the better quality data exert a stronger influence on the realizations. Conversely, poor quality data do not force unrealistic stratigraphic relationships. In application to the Llagas subbasin lithologic data, assigned correlation for different driller's logs ranges between 0.3 to 0.7, depending on quality of lithologic description. Assigned correlation of 1.0 was ascribed only to lithologic logs carefully described by hydrogeologists.

3.2. Isotopic Age Dating and Source Identification of Groundwater

Groundwater "age" represents the mean amount of time a groundwater parcel has resided in the saturated zone, isolated from any connection with the atmosphere. Groundwater ages can be used to understand travel times along flow pathways between recharge locations and sampling points, which are typically wells [16]. The water parcels collected in such a sample may be widely distributed in terms of their ages, largely as a function of the sampling length of the screened interval and dispersion and diffusion along flow pathways that reach the well [16].

Groundwater ages can be estimated from a combination of isotopic dating approaches: (1) tritium- ^3He ratios, based upon the amount of ^3He ingrown from the radioactive decay of tritium (an isotope of hydrogen incorporated in some water molecules), can be used to estimate the age of groundwater less than 50 years old; (2) raw tritium concentrations can be decay-corrected according to the tritium-helium age and compared with historical tritium concentrations in precipitation to indicate the fraction of water over 50 years old, and (3) radiogenic ^4He concentrations derived from the radioactive decay of uranium and thorium minerals in the subsurface can be used to estimate the age of the fraction of water over 50 years old.

In the Llagas subbasin, tritium- ^3He and ^4He groundwater age estimates were obtained from 13 wells (Fig. 5). In the Morgan Hill area, older tritium-helium ages generally correspond to older ^4He ages (Fig. 6). The younger tritium- ^3He age dates further refine wells vulnerable to water quality impairment. A sample from southeast Gilroy containing the youngest groundwater analyzed thus far may be influenced by recharge immediately to the west. Age versus depth relationships are difficult to infer because of long and multiple well screen intervals but stratified groundwater (younger, contaminated groundwater in the shallow section) is evident in wells with differing perforation intervals.

Several techniques can be used to infer the source of groundwater at a sampling point, or the source of nitrogen within the groundwater. For example, artificial recharge is being implemented in the northern portion of the Llagas subbasin using imported water from the San Francisco Bay Delta, which is fed by Sierra Nevada river flows. Because this water is depleted in its content of the ^{18}O isotope (incorporated in some water molecules), it is isotopically lighter than the recharge derived from local precipitation, and can be readily distinguished in groundwater. Recent ^{18}O measurements indicate that imported water is present in 6 of 12 wells sampled in the Morgan Hill area, while other wells in the Llagas

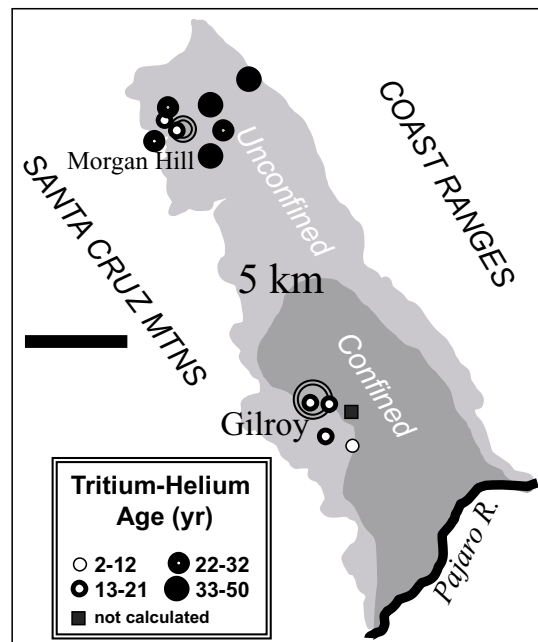


Figure 5. Tritium-helium groundwater age estimates for 13 samples obtained from Llagas subbasin.

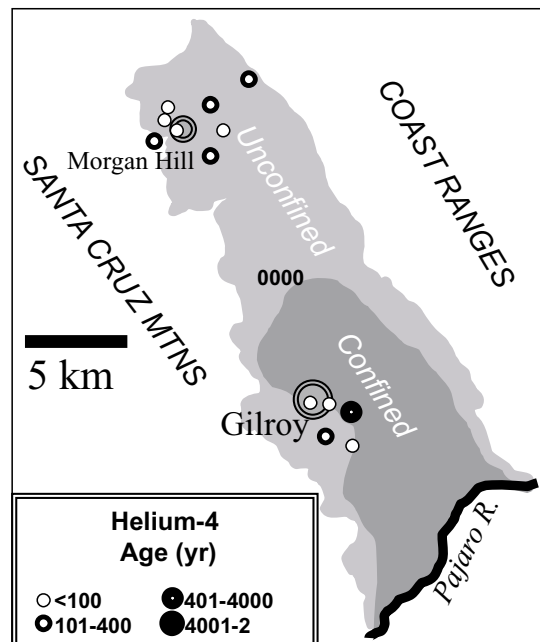


Figure 6. Helium-4 groundwater age estimates for 13 samples obtained from Llagas sub-basin.

subbasin indicate exclusively local recharge sources.

Measurements of dissolved air in groundwater samples (chiefly, Ar, N₂, and O₂) and the fraction of the nitrogen isotope ¹⁵N present can also be used to assess whether excess nitrogen exists as a product of microbial denitrification along an upgradient flow path, as well as correlate nitrate nitrogen with potential nitrate sources above the water table.

Altogether, groundwater age estimates larger or smaller than 100 years can help distinguish groundwater sources subject to anthropogenic effects. The use of groundwater age dates along with estimates of recharge sources, dissolved air, and dissolved nitrogen can help identify realistic lateral and vertical flow paths and travel times for flow models, as well as document the existence of denitrification and potential sources of nitrate along these flow paths. The flow models, in turn, may provide insights on actual age distributions and depth relationships to improve interpretation of isotopic age estimates [16]. This synergy is useful for identifying aquifer zones susceptible to contamination, including the past and future impacts from nitrate loading.

3.3. Geochemical Inverse Modeling

Geochemical inverse modeling can be useful in relating groundwater quality observations at specific locations to potential reactions occurring along upgradient flow paths or streamlines. For example, the inverse component of the PHREEQC geochemical modeling code [17] uses mass balance constraints imposed on chemical reactions to infer the probability of an assumed reaction mechanism. In the Llagas subbasin, such geochemical constraints can be used to identify and check plausibility of reaction mechanisms along putative flow paths subject to nitrate loading. For example, oxidation reactions entailing suspected nitrate sources, such as animal fertilizers, will produce measurable changes in aquifer chemistry (e.g., increases in dissolved inorganic carbon, declines in pH, and elevated calcium and magnesium concentrations associated with carbonate mineral dissolution).

In Figure 7, nitrate concentrations show correlation with total calcium and magnesium concentration from several samples collected in the Llagas subbasin. The nitrate data appear to be clustered with respect to sodium concentration, a good indicator of total dissolved solids. The separation of the nitrate data with respect to total dissolved solids provides some means, albeit crude, for distinguishing different recharge sources and flow paths and, therefore, different nitrate sources. In the figure, three reaction mechanism models are compared that involve (1) organic fertilizer (e.g., C₅H₇O₂N), (2) chemical fertilizer (e.g., NH₄N₃), and (3) equal contributions of nitrogen from organic and chemical fertilizers on a molar basis (Combo). Comparison of the data to the models indicates that mixing of recharge water and nitrate loading subject to different reaction mechanisms contributes to the observed concentrations.

3.4. Microbial Processes

Microbially facilitated denitrification reactions will be incorporated into our transport model as field and laboratory data are gathered and interpreted. In addition to field

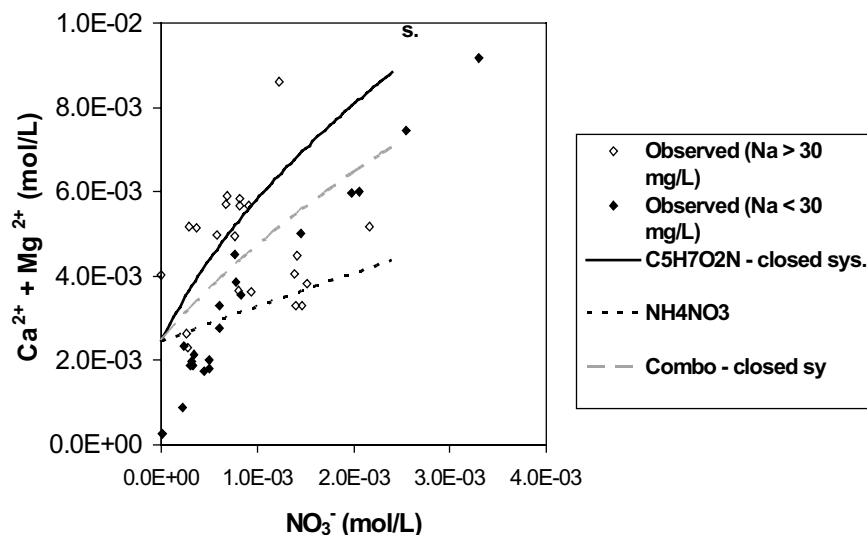


Figure 7. Comparison of nitrate to total calcium and magnesium concentrations, with possible nitrate source mechanism models.

data related to the identification of excess N_2 nitrogen in groundwater, two primary kinds of biological data will be used to address denitrification kinetics: (1) populations of denitrifying bacteria in aquifer samples collected in the field and (2) specific denitrification rates (i.e., mass of nitrate reduced per bacterial cell per unit time) determined in laboratory studies. To determine populations of denitrifying bacteria in field-collected aquifer samples, we will use quantitative, real-time PCR (Polymerase Chain Reaction) analysis that targets a diagnostic denitrification gene; based on an average of one gene copy per bacterial cell, the population of denitrifying bacteria in the sample can be calculated. Specific denitrification rates will be determined for the two major classes of denitrifying bacteria: heterotrophs and chemolithoautotrophs. Heterotrophic denitrifying bacteria use dissolved organic compounds as electron donors and as sources of cell carbon. Chemolithoautotrophic denitrifying bacteria, which can dominate denitrification activity in subsurface environments that are oligotrophic (i.e., low in organic carbon), use reduced inorganic compounds as electron donors and carbon dioxide as a source of cell carbon. As has been documented at numerous field sites, chemolithoautotrophic bacteria in aquifers often use reduced iron- and/or sulfur-containing minerals (such as FeS or FeS_2) as electron donors (e.g., [18]); such use of insoluble electron donors can render denitrification rates much slower for chemolithoautotrophs than for heterotrophs.

4. FLOW AND REACTIVE TRANSPORT MODELS

4.1. Hierarchical Flow Modeling Approach

Within the Llagas subbasin, two types of flow models will be considered. Initially, a subbasin-wide model will be developed in order to reconcile the basic water balances in the system (natural and artificial recharge, pumping and natural discharge, groundwater age, and water levels), both in terms of their current and historical configurations. This model will encompass confined and unconfined zones in the subbasin (e.g., as in Fig. 4), and will incorporate a vadose zone component to improve coupling of recharge processes to groundwater flow. The model will also be sufficiently detailed to resolve and distinguish the geostatistical variability of hydrofacies identified in Fig. 4 (2.8 million nodes). Codes such as Parflow [16,20] or NUFT [19] are being considered for this model.

More detailed, highly resolved submodels may be constructed in smaller portions of the subbasin volume, such as in the southern confined zone, as a means to more carefully study the effects of small-scale heterogeneity on transport and potential denitrification behavior. These models will be bounded by hydraulic conditions inferred from the subbasin model and will involve more highly resolved geostatistical detail within the three primary hydrofacies. Multi-million node simulations with Parflow will be required for these flow solutions.

Development and application of these models will be guided by isotopic age dating measurements, related groundwater and nitrogen source information, and inverse geochemical models. Apparent flow pathways inferred from these data must be reconciled with model simulations and the lithologic framework developed from the well observations. Conversely, the flow model and related transport simulations (below) will provide an important flow-path oriented framework for interpreting the isotopic measurements themselves, which are often derived from “mixed” water samples collected from wells with large screened intervals [16].

4.2. Hierarchical Transport Modeling Approach

Two types of transport models will be used in conjunction with both of the flow models mentioned in the previous section. On one level, particle based transport models (e.g., [21]) can be used to explore advection, dispersion, and time-of-flight (residence time) behavior for a small number of unreactive components in groundwater – such as nitrate or labeled recharge – and they can also be tailored to treat some types of simplified reactions, including denitrification.

To address more complicated behavior involving the transport and reaction of multiple dissolved species, especially in highly resolved flow systems, we will utilize a streamline-based reactive transport model. In this approach, a three-dimensional transport problem is recast into a large number of independent one-dimensional reactive transport simulations that correspond in a one-to-one fashion to a large number of streamlines that have been extracted from a three-dimensional flow field (e.g., [22,23]). The streamline mapping procedure involves a regridding process tailored specifically for transport simulations.

In many cases, this approach can drastically improve computational efficiency because (1) one dimensional transport problems are inherently easier to solve, (2) solutions on different streamlines can be obtained in parallel, and (3) computations may be focused in subsections of the flow domain where transport is of specific interest. In addition, the particular one-dimensional reactive transport model can be selected independently, such as PHREEQC [17], and used to represent, for example, aqueous complexation, oxidation-reduction processes, interphase transfer reactions (mineral precipitation and dissolution, ion exchange, and evolution of generated gases), and denitrification. The approach is largely limited to steady flow applications in which the importance of cross-streamline mass transfer (e.g., via transverse dispersion) is minimal.

4.3. Nitrate Migration and Fate

Ultimately, these models will be applied and tested iteratively to resolve and forecast nitrate loading and migration from one or more potential source areas, as documented in [8]. We expect to obtain improved perspectives and understanding of (1) the overall residence times of nitrate in the subbasin, especially as they pertain to selected source types, source locations, and proposed mitigation measures, (2) the potential role of denitrification as a sink mechanism for nitrate in the subbasin, in addition to natural discharge pathways, and (3) the potential for deeper zones of the subbasin to become contaminated with nitrate as a function of increased groundwater production in the future.

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High-Resolution Simulation of Basin Scale Nitrate Transport Considering Aquifer System Heterogeneity

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Geosphere

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High-Resolution Simulation of Basin Scale Nitrate Transport Considering Aquifer System Heterogeneity

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ABSTRACT

Nitrate contamination presents a growing threat to many groundwater basins relied upon for drinking water. This study combines geostatistical techniques, parallel computing of flow simulation, and particle tracking to develop realistic nitrate loading and transport scenarios. The simulation scenarios are patterned after the rapidly urbanizing Llagas groundwater subbasin in the south San Francisco Bay Area of California. In the Llagas subbasin, groundwater is the sole municipal water supply. A key component of this study is development of a highly-resolved model of the heterogeneity in the aquifer system using a new geostatistical technique for simulating hydrofacies architecture that can incorporate uncertain or “soft” data such as well driller logs. Numerical simulations of nitrate transport indicate the degree to which a heterogeneous conceptual model can account for dispersion relative to a conventional homogeneous model assuming typical dispersivity coefficients. The heterogeneous model transport results are found to be consistent with observed nitrate contamination patterns and

depth distribution as well as groundwater age trends with depth. The model provides a realistic test-bed for prediction of future nitrate concentrations, including the timeframe for potential nitrate impacts to deep wells given that geochemical data indicate denitrification is not likely to occur.

Keywords: geostatistics, simulation, nitrate, heterogeneity, geochemistry.

INTRODUCTION

Nitrate contamination of surface and groundwater is a pervasive and growing problem in the nation and in the world. High levels of nitrate affect both human and ecosystem health. High nitrate in drinking water is regulated because it has been associated with methemoglobinemia or “blue baby syndrome” (Johnson and Kross, 1990). High nitrate in surface and coastal waters leads to eutrophication. The human activities that contribute nitrate to groundwater – animal operations, crop fertilization, wastewater treatment discharge, and septic systems – are a legacy of commerce and growth over the last half-century yet are likely to continue into the future. Nitrate loading from these activities has increased significantly in the past 60 yr. Since 1945, U.S. population, which is correlated to wastewater treatment and septic system use, has more than doubled; synthetic nitrate fertilizer use has increased 20-fold; commercial cattle production has doubled, and poultry production has increased ~100-fold. More specialized and efficient animal production has created more and larger confined animal feeding operations on the majority of livestock or poultry farms with sales greater than \$100,000 (Natural Resources Conservation Service, 2003).

In California, greater than 40 percent of the State’s population uses groundwater for at least a portion of their public-supply needs. About 10% of California public drinking water supply wells produce water that exceeds the regulatory drinking water standard (10 mg/L as N),

and a much larger fraction produce water that approaches the limit (Fig. 1). Since 1984, ~8,600 of 25,000 drinking water supply wells have been shut down because of excessive nitrate. As the population of California increases by 50% over the next 20 yr, largely by urbanization of agricultural areas, water resources will be further stressed, and the loss of drinking water supply to nitrate contamination will become an increasingly serious water supply issue (Anton et al., 1988; Esser et al., 2002). As California moves increasingly to using groundwater basins to store water in lieu of above-ground reservoirs, nitrate contamination may become a severe water storage capacity issue (California Department of Water Resources [CDWR], 2003)

Groundwater quality problems, particularly nitrate, are increasingly being viewed from a basin-scale perspective. Prediction of contamination trends in groundwater is particularly problematic because aquifer systems have long response times (years to centuries), and are heterogeneous and difficult to characterize. Even with precise knowledge of land use and source loading history, prediction of impacts to groundwater is highly uncertain (McLay et al., 2001; Thorsen et al., 2001) and would likely require site controlled field experiments to decipher site-specific impacts to wells (Harter et al., 2002). These uncertainties magnify when modeling transport of reactive contaminants. The biogeochemistry of nitrate has a significant role on its transport: under oxic conditions, nitrate does not appreciably sorb and generally behaves conservatively; under anoxic conditions, however, nitrate can undergo denitrification, the biogeochemical process of converting nitrate to harmless molecular nitrogen. The effect of denitrification on nitrate transport can be difficult to characterize or predict over field to basin scales.

Numerical models offer means to predict long-term transport and future occurrence of nitrate contamination in aquifer systems, but realistic model implementation remains a challenge.

In addition to source uncertainties, the impacts of subsurface heterogeneity, hydrogeological processes (e.g., pumping and recharge patterns, ground-water flow, vadose zone processes), and denitrification need to be addressed. Some 2- and 3-D models have addressed denitrification in large-scale scenarios (Uffink and Romkens, 2001; Molenat and Gascuel-Oudou, 2002) but without explicit representation of aquifer system heterogeneity.

“Macrodispersion” or large-scale dispersion attributed to hydraulic heterogeneity is a major component to contaminant spreading in aquifer systems. Transport models typically use dispersivity coefficients or Gaussian random field representations to address macrodispersivity (Gelhar and Axness, 1983; Gelhar, 1986; Rubin, 1990; Tompson 1993). However, at the basin scale, heterogeneity associated with the spatial distribution of aquifers and aquitard units or “hydrofacies” within an alluvial basin will likely dominate basin-scale macrodispersion. In most basins, all heterogeneity associated with the “hydrofacies architecture” or hydrostratigraphy of the aquifer system cannot be represented deterministically. Yet, the heterogeneity will profoundly affect predictions of long-term impact to drinking water wells. These ideas are not new; the problem is how to account for heterogeneity and dispersion at the basin scale using commonly available characterization data and prior knowledge of the hydrogeology. As Bouwer (1991) states on the subject of macrodispersion, “As always, the main difficulty in dealing with heterogeneous media is characterization of underground conditions and simplification into manageable systems.” Further, once a realistic high-resolution multi-million cell hydrogeologic model is constructed, the problem remains to simulate flow and transport on a multi-million cell numerical grid.

This paper addresses impacts of basin-scale heterogeneity as follows:

- Abundant but uncertain “well driller log” data are incorporated as “soft data” in conjunction with accurate but less available lithologic data.
- Heterogeneity is explicitly accounted for by generating a geostatistical “realization” of aquifer system heterogeneity or “hydrofacies architecture.”
- High-resolution simulations of the flow field are computed using a robust and parallelized numerical simulation code.
- Non-reactive transport in the highly heterogeneous system is simulated using particle tracking.
- The high-resolution transport simulations are compared to lower-resolution simulations assuming homogeneity with effective dispersivity coefficients.

Rather than attempting to reproduce all historical nitrate sources and impact to wells in a basin, this study simply poses realistic nitrate transport scenarios related to historical agricultural use. The nitrate simulation scenarios assume non-reactive transport or unfavorable conditions for denitrification (e.g., oxic groundwater and/or lack of electron donor). Recently acquired geochemical and isotopic data show no evidence for saturated zone denitrification in the Llagas subbasin (Lawrence Livermore National Laboratory, 2005). Two scales of heterogeneity are considered: (1) hydrofacies related to aquitard, interbedded, and aquifer units, and (2) intermediate scale (2–20 m) hydraulic conductivity variability within the hydrofacies. Obviously, considerable heterogeneity occurs on smaller scales of meters or less. Much previous study has focused on determining effective dispersivity coefficients for longitudinal scales of hundreds of meters or less. Our basin-scale conceptual model assumes hydraulic conductivity variability associated with hydrofacies architecture will dominate basin-scale dispersion on scales of kilometers or more. Advantages of the high-resolution simulation approach over use of dispersion coefficients are:

- Fast pathways and fingering of plumes are resolved.
- The impact of large scale “matrix diffusion” or trapping of contaminants in low-hydraulic conductivity zones is accounted for in, for example, tailing of breakthrough curves and recalcitrance of residual contamination in source areas.
- The model of heterogeneity is consistent with field observations and prior knowledge of the hydrogeologic system.

The main goals of the high-resolution nitrate simulation are to better understand the long-term impact of nitrate loading to address basic questions such as:

- Although nitrate does not appear to impact deeper municipal wells today, is there a future threat?
- How much do location and depth affect vulnerability to nitrate contamination?
- If current levels of nitrate loading continue, will nitrate concentrations continue to increase?
- If major nitrate sources are eliminated, how will nitrate concentrations change?
- Is a simplified, low-resolution model sufficient to address long-term basin-scale nitrate issues?

In addition to nitrate transport, the scenarios presented could be modified to address other relatively non-reactive contaminants such as MTBE or perchlorate.

LLAGAS SUBBASIN STUDY AREA

The study area is the Llagas subbasin within the Gilroy-Hollister groundwater basin in California, located ~30 km south of San Jose, California (see Fig. 1). The 25 km-long northwest-trending Llagas subbasin is drained southward by tributaries of the Pajaro River, including Uvas and Llagas creeks which enter the alluvial basin near Gilroy and Morgan Hill, respectively. The water bearing materials in the subbasin consist of Pliocene to Holocene age unconsolidated to

semi-consolidated alluvial deposits (CDWR, 1981; Hoose, 1986). Average annual precipitation ranges from 40 cm the south to 60 cm in the north (CDWR, 2003).

The Llagas subbasin is bounded by the Santa Cruz Mountains to the west and the Coast Ranges to the east. The northern boundary is defined by a groundwater divide between the Coyote subbasin, which drains northward into the Santa Clara Valley basin. The Pajaro River forms the southern boundary. Given the wide range in size of groundwater basins, in general, this study regards the Llagas “subbasin” as within the lower size range for a “basin” scale.

Figure 1 also shows nitrate concentrations observed throughout the Santa Clara Valley basin and the Llagas subbasin. In the Santa Clara Valley basin, nitrate concentrations are generally below the maximum contaminant limit (MCL) of 45 mg/L (as NO_3^-). In the Llagas subbasin and the southern portion of the Coyote subbasin, however, nitrate concentrations are frequently observed above the MCL. In a study carried out by the local water agency, over 600 private domestic wells were tested for nitrate concentration, and more than 300 exceeded the MCL (Santa Clara Valley Water District, 1998).

In recent decades, the Llagas subbasin has undergone significant urbanization due to its proximity to the Silicon Valley and the south San Francisco Bay Area. Groundwater provides the sole source of water to most residential areas in the Llagas subbasin. Presently, nitrate contamination is prevalent in shallow zones. The threat of nitrate contamination to deeper zones where most public water systems obtain groundwater supplies is uncertain. The combined effect of dispersion and possible fast pathways between nitrate source areas and public wells is not well understood.

DATA

The flow model is based on commonly available hydrogeologic characterization and hydrologic data. Geochemistry data, including groundwater age, reveal major trends in nitrate source and spatial distribution over time.

Hydrogeologic Characterization

This and previous hydrogeologic interpretations depict hydrofacies architecture in Llagas subbasin as consisting of thin, gently dipping, and laterally continuous lenses composed of three principle hydrofacies: (1) coarse-grained aquifer materials associated with fluvial channel belts (2) fine-grained aquitard materials such as overbank and floodplain deposits, and (3) interbedded discontinuous layers of gravel and silt or clay (CDWR, 1981; Brown and Caldwell Geotechnical Consultants, Inc.; Hoose, 1986). These hydrofacies are related to fluvial depositional processes and, thus, geologic knowledge of fluvial depositional architecture can be used to advantage to develop realistic models of hydrofacies architecture. For example, ancient channel belt systems will be relatively anisotropic in shape with elongation in the ancient direction of flow, whereas floodplain deposits are more extensive and isotropic in lateral directions.

The richest source of data for constructing the hydrofacies architecture is found in “well driller logs”, which are understandably of variable quality. Landon and Belitz (1991) and Burow et al. (2004) give examples of the usefulness of well driller logs for large-scale hydrogeologic characterization in California with recognition of the limitations of these data. Over 300 well driller logs (Fig. 2) are used in this study to provide “soft conditioning” to geostatistical realizations as described below. High-quality lithologic descriptions are also available for several boreholes. For this study, well driller logs and other borehole lithologic descriptions were categorized according to hydrofacies with a degree of uncertainty.

The uncertainty in hydrofacies classification using well driller log data was quantified by assigning a correlation value to each log. The correlation value reflects an estimation of the correlation between the well driller log and reality. Thus, the correlation value could range between 0.0 (no correlation to reality) and 1.0 (perfect correlation to reality). Ideally, one could calculate the correlation value by comparing a well driller log to a high-quality lithologic log located a short distance away, then assign that same correlation value to other well driller logs of similar quality. Unfortunately, no such direct comparisons of well driller logs and high-quality lithologic logs were available. For this study, hydrofacies interpretations from the well driller logs were assigned correlation values between 0.3 and 0.7 based on expert opinion of the quality of lithologic description. These correlation values are used by the geostatistical simulation algorithms (summarized below) to treat well driller log data as uncertain or “soft” data. A few high-quality lithologic logs were included into the data set, and these data were assigned correlation values of 1.0.

Hydrology

Water level elevations indicate an overall southeasterly groundwater flow direction. Figure 3 shows generalized water level contours for Spring 2001 water level data (Santa Clara Valley Water District, 2002). Figure 3 also shows that groundwater conditions are regarded as unconfined in the northern and upland areas of the subbasin and confined in the central southern portion of the basin. Groundwater recharge occurs primarily in the unconfined portions of the subbasin near and south of Morgan Hill and immediately south and west of Gilroy.

CDWR conducted a detailed study of the Llagas subbasin (CDWR, 1981). In this previous study, CDWR developed a simple one-layer groundwater model with 38 cells in the Llagas subbasin. We use the CDWR model’s average annual cell-by-cell “stream infiltration”

values and average precipitation values to quantify magnitude and location of recharge for our high-resolution groundwater model.

Geochemistry

Historically, nitrate contamination is greatest in wells east of the valley axis, in the central and southern portions of the subbasin, where a large fraction of the wells have had concentrations above the MCL of 45 mg/L as NO_3^- (Fig. 1). In a study carried out by the local water agency, about half of over 600 private domestic wells tested for nitrate concentration exceeded the MCL (Santa Clara Valley Water District, 1998). Deep, high capacity public drinking water wells have lower, but slowly rising nitrate concentrations. This is a serious water supply problem because the region relies exclusively on groundwater for its drinking water, and at least 19 public supply wells are in the contaminated portion of this basin, although none has as yet exceeded the MCL.

Geochemical analyses of well water samples for major anions and cations, nitrogen and oxygen isotopes of nitrate, dissolved excess nitrogen, tritium and groundwater age, and trace organic compounds, indicate that synthetic fertilizer is the most likely source of nitrate in highly contaminated wells (Lawrence Livermore National Laboratory, 2005). In wells with nitrate concentrations greater than 40 mg/L nitrate- $\delta^{15}\text{N}$ values fall between 3.8‰ and 6.6‰. This range is covered by reported ranges for mineralized inorganic fertilizers and soil organic N, but not by animal wastes or precipitation. Current and historical data consistently show nitrate concentrations that are higher in shallow monitoring and domestic wells than in deep production wells. Several geochemical parameters (dissolved oxygen, tritium, and some major ions) also exhibit vertical stratification. Chemically stratified groundwater could be the result of a transition from oxidizing to reducing conditions at depth, in which case denitrification could potentially

account for the observed drop in nitrate concentrations. However, nitrate- $\delta^{15}\text{N}$ and $-\delta^{18}\text{O}$ isotopic compositions and absence of excess nitrogen are not consistent with denitrification being a significant process in the fate of nitrate in the subbasin (except in an area of recycled water application).

Tritium concentrations and tritium-helium age data reveal a very dynamic shallow aquifer flow system, with significant recharge and relatively rapid groundwater flow over a large part of the subbasin. Wells screened exclusively in deeper aquifers are devoid of tritium, indicating that the groundwater produced from those zones recharged more than fifty years ago (Lawrence Livermore National Laboratory, 2005).

METHODS

The area encompassed by our geostatistical and numerical flow and transport models is shown in Figure 3. The model area includes most of the Llagas subbasin. The most northerly portion of the subbasin was excluded as a simplification to better approximate confined flow conditions prevalent in the south. The version of the ParFlow code used for this high-resolution multi-million cell flow simulation is restricted to confined and steady-state flow conditions. The geostatistical and flow and transport simulation methods are summarized below along with necessary details on integration of “soft” data (e.g., well driller logs) within the geostatistical algorithm.

Transition Probability–Markov Geostatistics

The key step in the model development is to generate a highly resolved and realistic simulation of the alluvial heterogeneity in the subbasin. This study uses the transition probability–Markov geostatistical approach described by Carle and Fogg (1996), Carle (1997), and Carle and Fogg (1997) and applied by Carle et al. (1998), Fogg et al. (1998), Weissmann et

al. (1999), Thompson et al. (1999), Weissmann et al. (2002), Maxwell et al. (2003), and (Jones et al., 2005). This study adds implementation of a new approach to incorporate uncertain or “soft data” such as well driller logs. Carle (2003) gives more details on derivation, application, and validation of the “soft data” geostatistical approach.

To summarize, the transition probability/Markov geostatistical approach involves quantification of the spatial variability of categorical variables (e.g., hydrofacies) using the transition probability as a bivariate spatial statistic in lieu of indicator cross covariances or variograms as proposed by Deutsch and Journel (1992). Markov chain models of spatial variability are developed for each depositional direction (e.g., dip, strike, and upward) then combined into a 3-D Markov chain model (Carle and Fogg, 1997). The 3-D Markov chain model is used in a two-stage conditional simulation algorithm:

- (1) Generation of an initial hydrofacies configuration using the sequential indicator simulation algorithm (Deutsch and Journel, 1992) but reformulated with transition-probability based cokriging (Carle and Fogg, 1996), and
- (2) Simulated quenching (zero-temperature simulated annealing) with an objective function to minimize mean squared difference between simulated and modeled transition probabilities (Carle, 1997).

The simulation algorithm can also account for variations in depositional direction using pre-determined dip and strike angles, as shown by Carle et al. (1998), Thompson et al. (1999), and Weissmann et al. (1999). Variable dip and strike angles are applied in this study’s application to the Llagas subbasin. Figure 4 shows a geostatistical realization generated for this study. Steep dip angles are present toward the east. Variable directions of depositional strike are evident on the top surfaces.

Transition Probability

A transition probability matrix provides a relatively simple quantitative model to describe a pattern of spatial heterogeneity. An entry $t_{jk}(\mathbf{h})$ in a transition probability matrix $\mathbf{T}(\mathbf{h})$ is defined by

$$t_{jk}(\mathbf{h}) = \Pr\{k \text{ occurs at } \mathbf{x} + \mathbf{h} \mid j \text{ occurs at } \mathbf{x}\} \quad (1)$$

where j and k are categories (e.g., facies, classifications), \mathbf{x} is a location, and \mathbf{h} is a “lag” or separation vector.

The transition probability has long been used by geologists to analyze vertical successions (Vistelius, 1949; Krumbein and Dacey, 1969; Doveton, 1971; Miall, 1973). Figure 5 shows vertical transition probability measurements obtained for hydrofacies data with assumed correlation values of 0.7–1.0.

Markov Chain Model

The Markov chain is a stochastic (probabilistic) model that can be applied to a transition probability statistics as in (1). Conceptually, a one-dimensional Markov chain model assumes that an outcome depends entirely on the closest datum. For example, as applied to a vertical succession of facies, a Markov chain model assumes the probability of the next higher facies occurrence depends entirely on what facies occurs immediately below. Mathematically, the one-dimensional spatial Markov chain model formulates a transition probability matrix $\hat{\mathbf{T}}(h_\phi)$ as a matrix exponential

$$\hat{\mathbf{T}}(h_\phi) = \exp \mathbf{R}_\phi h_\phi$$

where h_ϕ is the lag in the ϕ direction and \mathbf{R} is the “transition rate matrix” in units of $[\text{length}]^{-1}$.

The matrix exponential is computed by eigenvalue decomposition, such that each transition probability model $\hat{t}_{jk}(\mathbf{h})$ for hydrofacies j and k consists of a linear combination of exponential functions and the assumed proportions (Agterberg, 1974).

The transition probability/Markov concepts can be extended laterally (e.g., depositional dip and strike) to formulate three-dimensional (3-D) Markov chain models $\hat{t}_{jk}(\mathbf{h})$ for any lag vector \mathbf{h} in any direction (Switzer, 1965; Carle and Fogg, 1997). The 3-D Markov chain is used in both the cokriging and simulated quenching steps of the geostatistical simulation algorithm to produce a “realization” of “hydrofacies architecture” (Carle et al., 1998).

Typically, data are abundant for characterizing vertical spatial variability of lithology. The transition probability measurements guide fitting of the “upward” or z-direction Markov chain model shown in Figure 5. Hydrofacies categories are ordered in the matrices as (1) aquitard, (2) interbedded, and (3) aquifer. The fitted model assumes that the upward successions of hydrofacies are statistically random:

$$\mathbf{R}_z = \begin{bmatrix} -1/4.0 & * & R \\ * & * & * \\ R & * & -1/3.0 \end{bmatrix} \mathbf{m}^{-1}$$

Where:

- proportions are [aquitards = 0.391; aquicludes = 0.329; aquifers = 0.280],
- 4.0 m and 3.0 m denote mean z-direction lengths,
- “ R ” denotes a random juxtapositional tendency, and
- “ $*$ ” invokes application of row and column summing constraints according to probability theory (Agterberg, 1974; Carle and Fogg, 1996) to compute the “interbedded” category model parameters.

Infusion of Geologic Interpretation

Lateral spatial variability is more difficult to characterize directly from data because of insufficiently close data spacing and uncertainties in vertical and angular control (e.g., depositional dip and strike). However, Markov chain models are readily developed from prior knowledge of facies architecture. Diagonal transition rates are directly related to facies mean lengths, and off-diagonal transition rates are directly related to juxtapositional tendencies – the frequency at which facies occur adjacent to each other. In this study, the transition rate matrices for the x (strike) and y (dip) directions were developed as follows:

Proportions: [aquitards = 0.391; aquicludes = 0.329; aquifers = 0.280]

$$\mathbf{R}_x = \begin{bmatrix} -1/2500 & * & 0.5/2500 \\ * & * & * \\ S & * & -1/300 \end{bmatrix} \text{m}^{-1}$$

where

- proportions are [aquitards = 0.391; aquicludes = 0.329; aquifers = 0.280],
- 2500 m and 300 m denote the mean x -direction lengths of aquitards and aquifers,
- 0.5 indicates the probability of an aquifer being juxtaposed to an aquitard in the $+x$ direction;

and

- “ S ” indicates an assumption of symmetry.

$$\mathbf{R}_y = \begin{bmatrix} -1/5000 & * & 0.0 \\ * & * & * \\ 0.0 & * & -1/1000 \end{bmatrix} \text{m}^{-1}$$

where:

- 5000 m and 1000 m denote the mean y -direction lengths of aquitards and aquifers, and

- the “0.0” off-diagonal entries are placed to prevent aquifers and aquitards from linking together in the “downstream” direction.

Note that the x and y direction mean length ratios indicate the degree of lateral anisotropy in the hydrofacies geometry. For example, the aquifer hydrofacies $y:x$ mean length ratio of 10:3 is related to the assumption of aquifers derived from channel belt deposition with the “ y ” direction aligned in the major direction of flow.

Integration of Soft Data

This study utilizes a novel approach to integrate soft data into the two-step stochastic simulation method. The integration of soft data is implemented by modifying both (1) the cokriging equations for the sequential indicator simulation step and (2) the decision-making process for changing categories at individual grid cell locations as performed within the simulated quenching step.

Cokriging

The cokriging system of equations is used to estimate the probability that a facies occurs at a certain location given the occurrences of facies at surrounding locations (e.g., data or previously simulated grid cells). In application to stochastic simulation, the “sequential indicator simulation” (SIS) algorithm (Gomez-Hernandez and Srivastava, 1990) incorporates conditional probability estimates to select the simulated facies at cell locations along a random path. Carle and Fogg (1996) show that “indicator” (categorical) cokriging equations can be formulated with transition probabilities, such as a Markov chain model, to approximate the conditional probability estimates. To account for soft data, the transition probabilities entered into the cokriging equations should be modified to reflect the uncertainty of the data. This can be

accomplished by substituting $\tilde{t}_{jk}(\mathbf{h})$ in place of $\hat{t}_{jk}(\mathbf{h})$ into the cokriging equations, with

$\tilde{t}_{jk}(\mathbf{h})$ defined as

$$\tilde{t}_{jk}(\mathbf{h}) = \alpha(\mathbf{x})\alpha(\mathbf{x} + \mathbf{h})\hat{t}_{jk}(\mathbf{h}) + [1 - \alpha(\mathbf{x})\alpha(\mathbf{x} + \mathbf{h})]p_k$$

where:

$\alpha(\mathbf{x})$ = correlation value of data located at \mathbf{x}

$\hat{t}_{jk}(\mathbf{h})$ = entry in the Markov chain model transition probability matrix for lag \mathbf{h} .

p_k = probability that k occurs in the domain interest (stationary or global probability).

In formulating the cokriging equations with $\tilde{t}_{jk}(\mathbf{h})$ for the SIS algorithm, only soft data locations are assigned correlation values less than unity; previously simulated locations or hard data locations assume correlation values of unity. Throughout the cokriging step, the soft data categories remain unchanged to allow the cokriging step to impart structure conditional to the soft data and associated correlation values. Soft data can be changed in the simulated quenching step as described below.

Simulated Quenching

Because a cokriging (or indicator kriging) estimate is not an exact solution to the conditional probability that a facies occurs at a location given surrounding data, a second “simulated quenching” step is recommended. The simulated quenching step attempts to minimize an objective function defined as the squared difference between calculated and modeled transition probabilities (Carle, 1997). The simulated quenching step is also used at soft data locations to address the uncertainty of the data. As the correlation value of the soft data decreases, the simulated quenching step enables the simulation algorithm to weigh more toward

using the model of spatial variability and less toward using the soft data value to select a category at a soft data grid location.

During implementation of the simulated quenching algorithm, the objective function is reduced through change of categories at individual grid cell locations along a random path. The change of category that reduces the objective function the most is accepted. If no change reduces the objective function, no swap is performed. To consider soft data, the correlation value is used to prescribe a probability that the category change will be rejected. If the correlation value is 1.0, a category change will always be rejected to honor “hard” data. If the correlation value is 0.0, a category change that reduces the objective function will always be accepted. If the correlation value is 0.7, for example, a category change will be rejected with 30% probability. In this manner, the correlation value is used to permit facies changes in the realizations proportionately to the degree of certainty in the data. Through comparison of simulation results at and near data and simulated and modeled transition probabilities, Carle (1997) and Carle et al. (1998) provide validation of the transition probability/Markov stochastic simulation approach, while Carle (2003) provides additional testing and validation for consideration of soft data.

Flow and Transport Simulation

Once a geostatistical model is developed, it is not difficult to generate multi-million cell geostatistical realizations and assign hydraulic properties to hydrofacies. Performing high-resolution flow and transport simulation presents a greater computational challenge.

Hydraulic Property Variation and Calibration

In the heterogeneous model, each hydrofacies is expected to exhibit spatial variability of hydraulic properties. On the heterogeneous model’s grid spacing of $(dx:dy:dz) = (2m: 20m: 20m)$, however, we assume that hydrofacies spatial variability between grid blocks is

uncorrelated. Each hydrofacies is assigned constant porosity and log-normally distributed hydraulic conductivity (K) as shown in Table 1. Figure 6 shows a geostatistical realization of hydraulic conductivity for Llagas subbasin, which was produced by superposing the hydrofacies hydraulic conductivity spatial distributions onto the hydrofacies realization shown in Figure 4. For the homogeneous model, constant hydraulic conductivity of 12 m/d and constant porosity of 0.3 are assumed. In both heterogeneous and heterogeneous cases, hydraulic conductivity is assumed to decrease with depth at a rate of 37% per 100 m vertical. Calibration to measured groundwater elevations (Figure 3) was accomplished by simple trial-and-error adjustment of the hydraulic conductivity of the homogeneous model and the geometric mean hydraulic conductivity of the aquifer hydrofacies in the heterogeneous model.

Flow Model

Another key step in this study is use of the robust and parallelized flow modeling code ParFlow, which is capable of solving multi-million cell problems for highly heterogeneous systems (Tompson et al., 1998; Tompson et al., 1999). ParFlow uses an efficient and scalable multigrid preconditioned conjugate gradient algorithm such that flow problems can be run on parallel platforms, and run times scale nearly linearly with problem size (Ashby and Falgout, 1996).

Boundary Conditions

Boundary conditions are critical to model conceptualization and calibration. The outer shell of the model is a no-flow boundary condition except for the northern, top and bottom boundaries. At the northern boundary, a prescribed flux (subsurface inflow) of 4.5×10^6 m³/year is assigned across the subbasin deposits based on average annual flux of the CDWR (1981) groundwater model. At the top boundary, an average annual rate of recharge of 5.0×10^7 m³/year is distributed

non-uniformly at locations consistent with the CDWR (1981) groundwater model. The principal areas of recharge are west of Gilroy (near model coordinates $x=0, y=10,000$) and toward the north, as evident by the distribution of higher hydraulic heads across the top the models shown in Figures 7 and 8. A flux of 4.5×10^6 m³/year is input to the northern boundary of the model to account for subsurface flow.

The no-flow boundary condition at the southern boundary (toward the Pajaro River) effectively assumes symmetry of flow with the Bolsa subbasin to the south. The Pajaro River is perched over thick aquitard units, and no groundwater discharge or recharge to the Pajaro River is assumed. Pumping rates for 102 wells are nearly balanced to the recharge. A constant general-head condition is applied beneath the southern portion of the model to approximate hydraulic communication with the deeper water-bearing Purisima Formation, which is composed of interbedded sandstone and siltstone of Pliocene age (CDWR, 1981).

Wells

The flow model contains 102 pumping wells. Locations of assumed screened intervals are projected as vertical lines in both Figure 7 and 8. Although many more wells are actually present in the Llagas subbasin, simplification of the model was necessary due to lack of complete well location and pumping data. Wells are categorized by depth range, with “shallow” wells defined by well screen depths above sea level, “intermediate” wells defined by well screen depths between 0 and 100 m below sea level, and “deep” wells defined by well screen depths deeper than 100 m below sea level. This well categorization results in 47 shallow wells, 46 intermediate wells, and 9 deep wells. Historical pumping rates were used where available. However, pumping rates at many wells, particularly shallow and intermediate depth wells, were

increased by a factor of 10 or more to compensate for the model's known under-representation of the total number of active wells in Llagas subbasin. All pumping rates are constant under the steady-state flow model assumption.

Particle Tracking

To simulate non-reactive transport in a mass-conservative, accurate, and computationally efficient manner, a Lagrangian particle tracking algorithm was used (Maxwell et al., 1999). Advective transport is simulated via a quasi-analytical streamline algorithm (Shafer-Perrini et al., 1991), while dispersive and diffusive transport is simulated by a random walk algorithm using bilinear velocity interpolation (Labolle et al., 1996). Particles are moved independently with optimized timesteps for particle movements. Particles are bifurcated in regions of low particle density.

The homogenous model assumes relatively large dispersivity coefficients of 10 m longitudinal and 1 m transverse, whereas the heterogeneous model assumes zero dispersivity. Assignment of fixed dispersivity coefficients is problematic because dispersivity increases with scale, although a 10 m longitudinal dispersivity coefficient is believed to be representative for some aquifers up to scales of multiple kilometers (Gelhar, 1986). Dispersion in the heterogeneous model is caused entirely by heterogeneity built into the hydraulic conductivity field.

Source Loading

The nitrate transport simulations are conducted as realistic hypothetical scenarios for a few likely sources based on past land use in the Llagas subbasin. However, the entire nitrate source loading history for the subbasin, including septic systems, is by no means accounted for. Suspected nitrate loading sources (with number of source locations) considered by this study are

dairies (3), poultry farms (2), greenhouse operations (2), and irrigated agriculture (2) (see Fig. 9). Based on estimates of nitrate produced by these types of farming (Santa Clara Valley Water District, 1994) and assuming increased nitrate loading over time between 1945 and 1985, a source loading curve was developed (see Fig. 10). The source loading curves arbitrarily do not consider any nitrate management practices and, therefore, are largely hypothetical. The most concentrated source of nitrate is assumed to be poultry farms. For practical purposes, however, the “dairy,” “poultry farm,” and “greenhouse” sources can be viewed as point sources covering a range of nitrate source loading rates, while the “irrigated agriculture” sources represent patch-shaped “non-point” sources. The source loading function assumes that the agricultural nitrate sources remain constant after 1985, except for the case of poultry farms. In this modeling scenario, the “poultry farm” sources impacting groundwater are assumed to cease in 2045.

Nitrate Transport Results

Two nitrate transport simulation scenarios are presented and compared: (1) a “homogeneous” case where the hydraulic conductivity field is assumed homogeneous and effective dispersion coefficients are implemented for transport simulation, and (2) a “heterogeneous” case where the geostatistical model defines a spatially variable hydraulic conductivity field. In both cases, the flow models are calibrated to head, well pumping is identical, and nitrate loading is identical. Visualizations of plume behavior and breakthrough curves are used to compare results from these two conceptual models of basin-scale nitrate transport.

Given that the nitrate loading scenarios are not comprehensive (particularly for irrigated agriculture), simulated breakthrough at the wells is expected to under-represent the total impact of nitrate loading in Llagas basin. The nitrate transport simulation results focus on the character

of well impacts and breakthrough curves under the assumption of a limited number of nitrate sources. These results aid understanding of long-term nitrate impacts and relationship to other observations such as geochemical and groundwater age data.

Flow

Figures 7 and 8 show simulated head for the homogeneous and heterogeneous cases, respectively, assuming steady-state flow. Hydraulic head is matched reasonably well in both cases to typical head values in the basin (e.g., Fig. 2). The models differ particularly in the west and south.

In the homogenous model, heads are too high (above 100 m) in the western recharge area because the relatively large proportion of coarse-grained deposits is not accounted for. The heterogeneous model, however, incorporates the known abundance of coarse-grained deposits in the western recharge area to achieve a more realistic calibration to local head. In support of this result, isotopic and groundwater age results delineate an area of active recharge and relatively rapid flow in the southwestern portion of the study area. In the south, heads are relatively uniform and higher in the homogeneous model because the increased proportion of fine-grained deposits is not accounted for. The heterogeneous model adapts the proportion of coarse and fine-grained deposits according to local lithologic data. Thus, it is possible to obtain a more realistic flow calibration with a geostatistical model by incorporating well driller log data as “soft data” to condition local spatial distribution of hydrofacies.

Dispersion

Although dispersion can be quantified through moment calculations, the basin scale dispersive effects from multiple contaminant loading sites and pumping locations can be better appreciated from visual inspection. Figure 11 shows evolution of nitrate concentration from

simulation times 1965, 2045, and 2145 yr (20, 100, and 200 yr after the beginning of nitrate loading) for both the homogeneous and heterogeneous conceptual models.

In comparing Figure 11 (a) and (b), already at 20 yr since the beginning of nitrate loading, the heterogeneous model shows distinct fingering in nitrate transport resulting in greater longitudinal (along flow direction) dispersion than the homogeneous model. In comparing Figure 11 (c) and (d) at 100 yr since nitrate loading began, not only increased longitudinal dispersion but also significant transverse dispersion is evident in the heterogeneous model. The western “irrigated agriculture” source exhibits a fan-shaped dispersion pattern not seen in the homogeneous model using dispersivity coefficients. In comparing Figure 11 (e) and (f), the heterogeneous model exhibits the character of much more pervasive nitrate contamination relative to the homogeneous model after two centuries of nitrate loading.

Another indicator of dispersion is how many of the 102 wells considered were impacted by the simulated nitrate loading. All nitrate sources are not accounted for in the transport simulations and, therefore, the criteria for “impacted” in the transport simulations must be considerably less than the MCL. Based on a criterion for breakthrough exceeding 0.1 mg/L (the approximate minimum concentration resolution of the transport simulations) for over 50 yr, 11 wells in the homogeneous model were impacted, and 18 wells in the heterogeneous model were impacted. Of the impacted homogeneous wells, four (18, 40, 43, and 50) were shallow (out of 47 total) and seven (27, 33, 41, 48, 51, 64 and 65) were of intermediate depth (out of 46 total). Of the impacted heterogeneous wells, nine were shallow (15, 16, 18, 32, 34, 43, 45, 46, 49, and 79), and nine were of intermediate depth (17, 27, 33, 41, 48, 65, 78, 82, 85, 88, 100). Figure 12 shows selected breakthrough curves. Notably, of the nine deep wells, two (79 and 86) exhibited a gradual, long-term breakthrough in the heterogeneous model. No deep wells in the homogeneous

model exhibited breakthrough. The result of more wells being significantly impacted by nitrate in the heterogeneous model indicates a greater degree of dispersion in the heterogeneous model compared to the homogeneous model using dispersivity coefficients. Certainly, one could increase the dispersivity coefficients in the homogeneous model to increase dispersion, although that will not address scale dependencies and structural characteristics (e.g., variation of anisotropy direction and dip angles).

Character of Breakthrough

The character of the breakthrough curves is useful to predict future trends such as the impact of eliminating a nitrate source (e.g., the hypothetical “poultry farms”), delay in impact relative to timing of source loading, and vulnerability of wells with respect to depth.

Figure 12 (a) and (b) show breakthrough curves for shallow wells in the heterogeneous and homogeneous model. Wells 18 and 43 show similar shapes in breakthrough for both the heterogeneous and homogeneous models, suggesting that a homogeneous model could account for heterogeneity-related impacts of dispersion in some cases. Upon closer inspection of Figure 11, wells 18 and 43 are located along the lateral periphery of the nitrate plumes.

Of the shallow wells, wells 32, 34, and 39 in the heterogeneous model and 33, 41, and 61 in the homogeneous model exhibit peaked breakthrough suggesting impact from the poultry farm sources (which terminate in year 2045). Wells 32, 34, and 39 are all located very close to the poultry farm sources. The breakthrough curves in Figure 12(a) suggest that removal of the poultry farm source would result in a near-immediate nitrate concentration decrease in these shallow wells over a time frame of 40–100 yr. Similarly, well 40 in the homogenous case shown in Figure 12(b) exhibits a rapid nitrate concentration decrease within a timeframe of 25 yr. Shallow well 50, however, shows a delayed response to the poultry farm nitrate source, with

peak breakthrough ~90 yr after termination of the poultry farm source. Interestingly, none of the shallow wells in the heterogeneous model exhibit a comparable delayed response. The difference in response can be attributed to the stratigraphic dip angles incorporated into the heterogeneous model. These dip angles cause the poultry farm source nitrate contamination to dive downward below apparently “downgradient” shallow wells.

Wells 18 and 43 in both models and wells 15, 16, and 46 in the heterogeneous model exhibit relatively stable long-term nitrate concentrations. This stabilization indicates that if loading sources remain constant, many shallow wells can be expected to exhibit a relatively constant long-term nitrate concentration. However, the breakthrough responses from wells 15, 16, 18 and 43 indicate that stabilization in nitrate breakthrough for shallow wells could lag by several decades behind the stabilization of nitrate loading.

Figure 12 (c) and (d) show breakthrough in intermediate depth wells. Breakthrough occurs in both the heterogeneous and homogeneous models for wells 27, 33, 41, and 65. Breakthrough for wells 27 and 65 is similar for both models, but quite different for wells 33 and 41. In the homogeneous model, wells 33 and 41 show similar peak breakthrough related to separate poultry sources. For well 33, the long-term stabilization indicates contribution from another source, most likely dairy. Well 51 exhibits delayed breakthrough from a distant poultry source in the homogeneous model, and no response in the heterogeneous model. In the heterogeneous model, multiple sources may be impacting well 33, while well 41 exhibits a “double-peak” indicating an initial impact from the closest poultry farm source and a later impact from a more distant poultry farm source, an impact not seen in the homogeneous model. Breakthrough in wells 78, 82, and 85 for the heterogeneous model is caused by the western

irrigated agriculture source. Breakthrough in wells 48 and 65 for the homogeneous model is caused by the central irrigated agriculture source.

Figure 12 (e) shows breakthrough for two deep wells, 79 and 86, in the heterogeneous model. The delayed, relatively low-magnitude breakthrough indicates that the deep, municipal wells could expect impacts from nitrate in the future given that denitrification is not likely to occur. However, only two of the nine deep wells showed any breakthrough over the course of the 500 yr long simulation. This, combined with the long gradual rise in nitrate concentration for the two impacted deep wells indicates that mean groundwater travel times to deep well screens would likely be on the order of centuries or more.

DISCUSSION

The transport simulation results for both the heterogeneous and homogeneous models are comparable to the general trends in nitrate contamination in Llagas basin. Based on hundreds of nitrate samples in Llagas basin, nitrate concentrations at individual wells have shown consistent upward trends since the 1960's (Santa Clara Valley Water District, 1994, 1998; Lawrence Livermore National Laboratory, 2005). These upward trending nitrate concentrations are prevalent at depths of 60–120 m, which corresponds to the shallow and upper immediate zones of this modeling study. Low tritium concentration and low nitrate are prevalent below depths of 110–120 m, which would correspond to deeper intermediate wells and portions of deep wells simulated in this study (Lawrence Livermore National Laboratory, 2005). The transition from shallow high nitrate to deep low nitrate groundwater could therefore be due to hydrogeologic factors; i.e., many shallow to intermediate depth wells combined with the presence of laterally extensive aquitards that have delayed mixing between recently recharged, nitrate contaminated groundwater above and relatively isolated old 'pristine' groundwater below.

The transport simulations and geochemical characterization both indicate that low tritium and low nitrate observations in relatively deep wells in Llagas basin can be explained by the presence of older groundwater rather than by denitrification. However, fast pathways related to heterogeneity could facilitate transport of a component of younger groundwater into deep wells with long screened intervals. Therefore, the heterogeneous model results are consistent with slow rising nitrate trends in deep wells where nitrate concentrations currently remain well below the MCL (Lawrence Livermore National Laboratory, 2005). This modeling study attributed a large proportion of the nitrate contamination in Llagas subbasin to dairy or poultry farm sources, while geochemical data suggest nitrate contamination in Llagas subbasin is primarily attributed to irrigated agriculture instead of manure sources (Lawrence Livermore National Laboratory, 2005). These discrepancies could be explained by either the model's under-representation of irrigated agriculture sources or structural effects (e.g., dip angles) in the eastern Llagas basin that could cause nitrate contamination to dive below most shallow and intermediate depth wells.

The simulation results of this modeling study are generally consistent with field observations, suggesting that nitrate does indeed behave conservatively in the Llagas subbasin. However, these modeling results have many limitations. Significantly, the assumption was made that the hydrogeologic conceptual model is correct, which involves several simplifying assumptions, such as:

- Facies-related heterogeneity patterns are statistically stationary throughout the basin (except for trends in proportions).
- Only one realization was examined.
- Structural assumptions, including depositional direction, deformation, and lack of fault displacement, are correct.

- Flow is steady-state and thus ignores seasonal and annual variation of recharge and pumping.
- Only a small portion of the shallow- and intermediate-depth wells is accounted for.
- The hydrogeologic complexities of the northern portion of the Llagas subbasin including the City of Morgan Hill and the northern boundary between Llagas subbasin and the Coyote subbasin north are not addressed.
- Only a small portion of irrigated agriculture is accounted for, and geochemical data indicate that irrigated agriculture may be the primary source of nitrate (Lawrence Livermore National Laboratory, 2005).
- Irrigation return flow is not accounted for.
- Only a small portion of total nitrate loading is accounted for, and that portion is highly simplified.
- Changing land use is not accounted for except for changing nitrate loading rates that either stabilize or terminate.
- Vadose zone processes are not accounted for.

The high-resolution, heterogeneous model was primarily constructed to demonstrate the capability to perform high-resolution groundwater basin-scale flow and nitrate transport simulations under a realistic scenario. However, by no means does this paper conclude that use of heterogeneous conceptual model to account for dispersivity is in all cases more appropriate than using dispersivity coefficients applied to a homogeneous conceptual model. Choice of conceptual model is certainly discretionary. In either the heterogeneous or homogeneous case, the modeling results suggest that calibration to both groundwater age and nitrate concentration trends will vastly improve long-term predictions of basin-scale flow and transport.

In the past, geostatistical techniques and computational capabilities were not available to perform high-resolution basin-scale simulation. Presently though, lithologic data of variable quality including well driller logs can be used through geostatistical techniques to help constrain and characterize 3-D heterogeneous flow and transport models. The practitioner now can choose between conceptual models incorporating explicitly heterogeneous or effective properties based on homogeneous assumptions. In some respects, a heterogeneous model can be more intuitive to construct because it can be made directly consistent with lithologic data and other geologic knowledge. A homogeneous model may require more effort in determining appropriate effective properties, which may or may not be realistic.

The heterogeneous hydrogeologic model presented in this paper could be improved by adding more lithologic data, particularly high-quality lithologic descriptions obtained by continuous or semi-continuous core, geophysical logs, or cone-penetrometer data. Hydrostratigraphic interpretations could be used to define packages of alluvial deposition instead of lumping the entire subbasin's alluvial deposits into one set of geostatistical parameters as was done in this study. Pump test data would be useful to refine the estimates of the hydraulic conductivity distributions for different hydrofacies. A transient flow model could be used, particularly a Richards Equation based model (Jones and Woodward, 2001) to better account for vadose zone, recharge, or irrigation return processes. The particle model could also be applied in a "backward" mode in time to reproduce groundwater age distributions at wells (Tompson et al., 1999). This could be particularly useful to calibrate a model to groundwater age data.

CONCLUSIONS

Given commonly available data such as well driller logs, well locations, and pumping rates combined with hydrogeologic interpretation, geostatistical techniques, parallelized flow and

particle tracking modeling codes, it is becoming computationally feasible to model basin-scale flow and transport at high resolution with multi-million cell numerical grids. It is possible to account for uncertainty in lithologic data to enable abundant well driller logs to influence, but not absolutely constrain, the distribution of hydrofacies in a geostatistical realization. Given conditioning data, the geostatistical model can account for differences in proportions of hydrofacies, such as more coarse-grained materials in proximal areas and more fine-grained materials in distal area. Prior structural knowledge such as dip and strike depositional or deformation directions can be incorporated into the basin-scale geostatistical realizations. Such structural information can influence prediction of transport behavior by, for example, causing contaminant migration to dive downward along a dipping bedding plane and miss an apparent downgradient receptor.

A highly-resolved heterogeneous numerical model can produce complex transport behavior that produces fingering and greater lateral and transverse dispersion compared to a conventional homogeneous model with typical dispersivity coefficients. Compared to a simplified homogeneous model, the heterogeneous model exhibits broader impact to wells from a fixed number of nitrate sources, including prediction of potential long-term impacts to deeper wells. A highly resolved basin-scale model can be used to evaluate impacts of past and future nitrate loading scenarios and to predict concentration trends and timing of peak breakthrough. As for all modeling of flow and transport, such a basin-scale model can greatly benefit from calibration or consistency-checking to groundwater age data. The highly-resolved groundwater flow and transport model developed in this study has yielded nitrate transport results that are consistent with existing geochemical and groundwater age data in the Llagas subbasin suggesting that denitrification is not significant. Future modeling work is needed to assess a more complete

inventory of nitrate source loading in Llagas basin, particularly for irrigated agriculture because recent geochemical data indicate synthetic fertilizer is the most likely nitrate source in highly contaminated wells.

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FIGURES

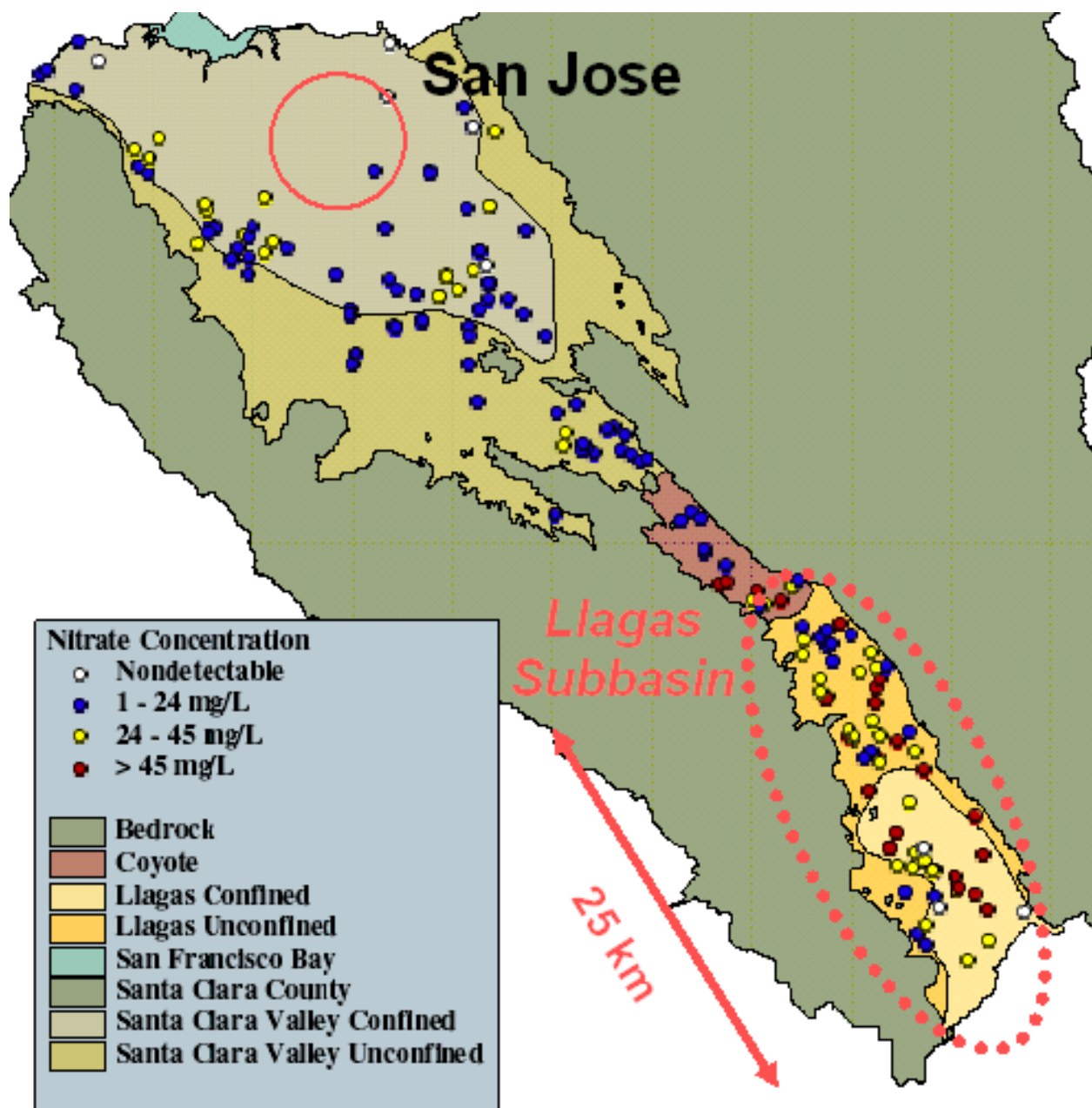


Figure 1. Map showing nitrate concentrations and location of Llagas subbasin in Santa Clara County, California relative to Santa Clara Valley and the City of San Jose (Santa Clara Valley Water District, 1998).

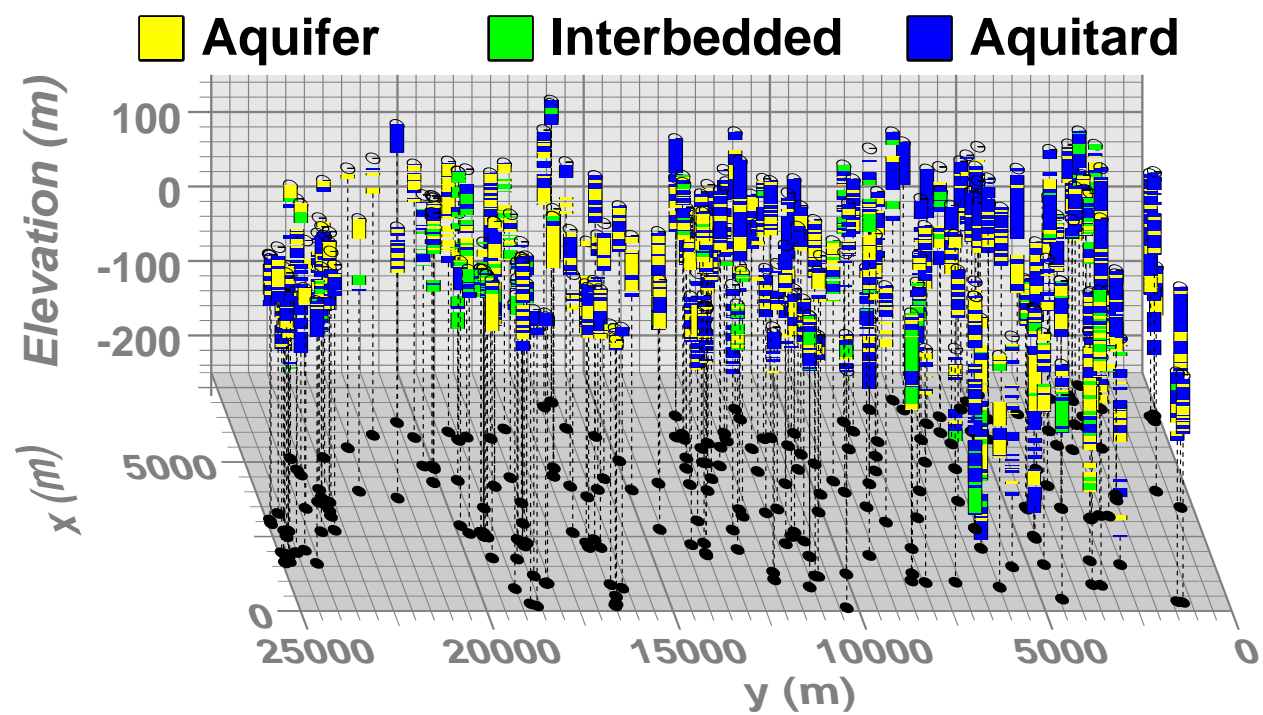


Figure 2. Posting of well driller log data used for this study. Data are categorized into aquifer, aquitard, and interbedded hydrofacies.

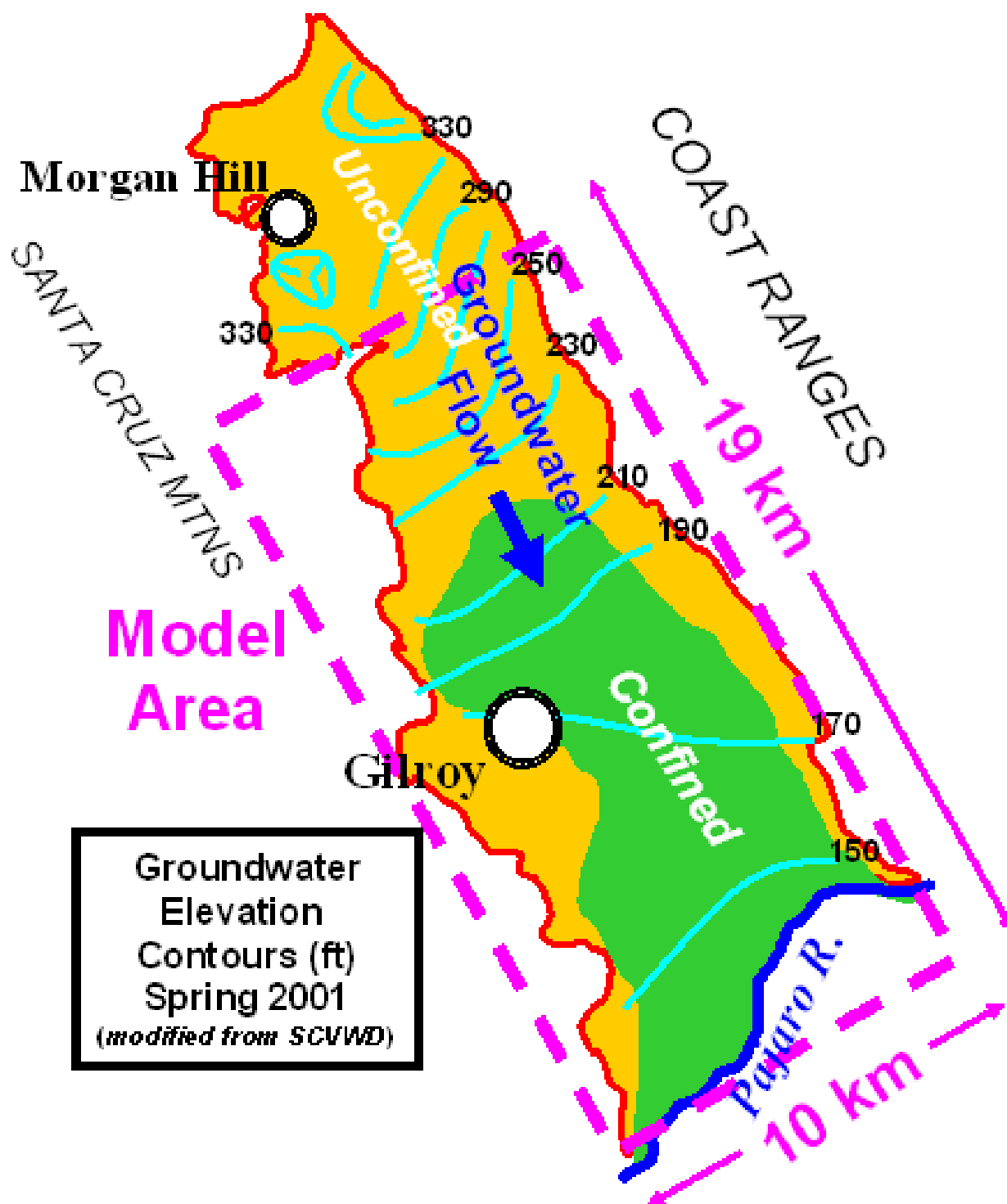


Figure 3. Outline of Llagas subbasin showing confined and unconfined groundwater flow regimes, flow and transport model area, and groundwater elevation contours for Spring 2001.

SCVWD—Santa Clara Valley Water District.

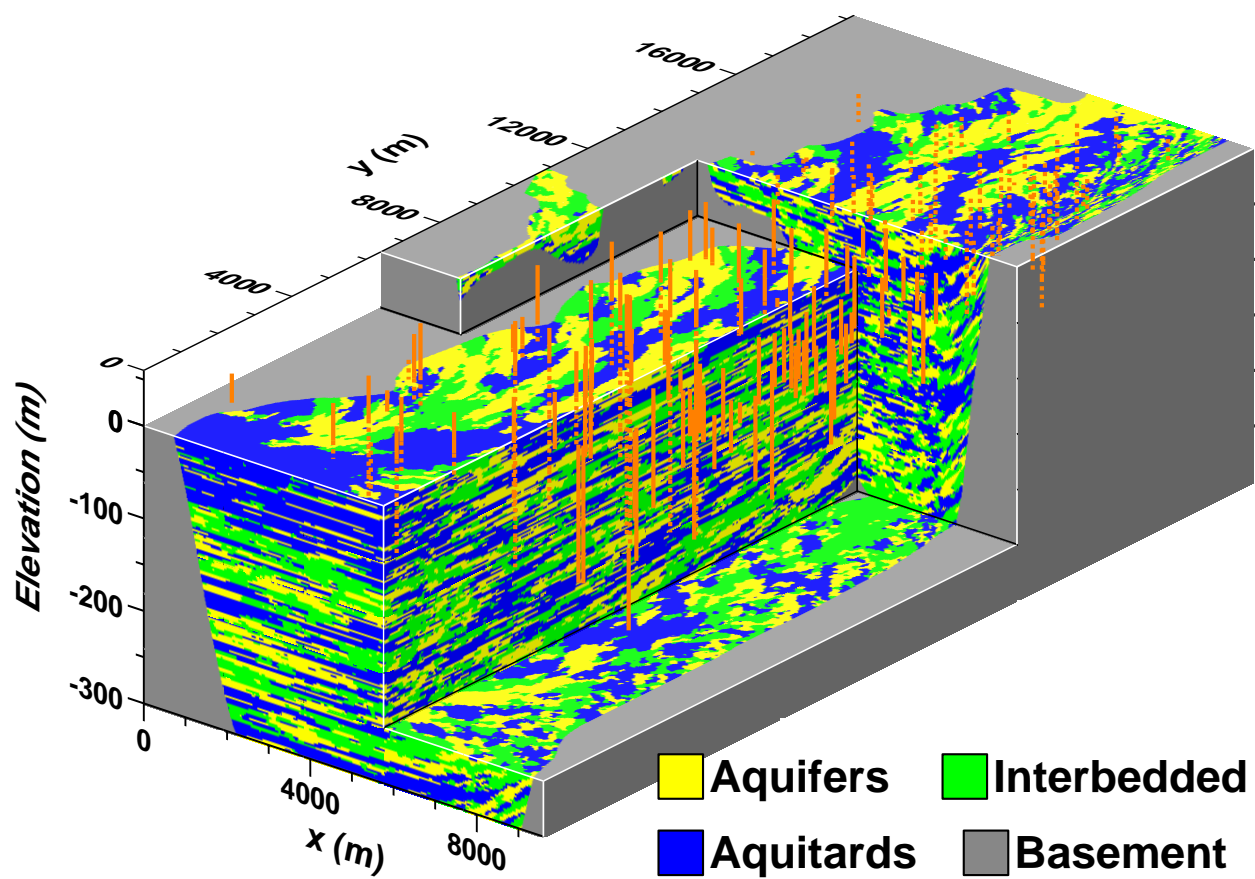
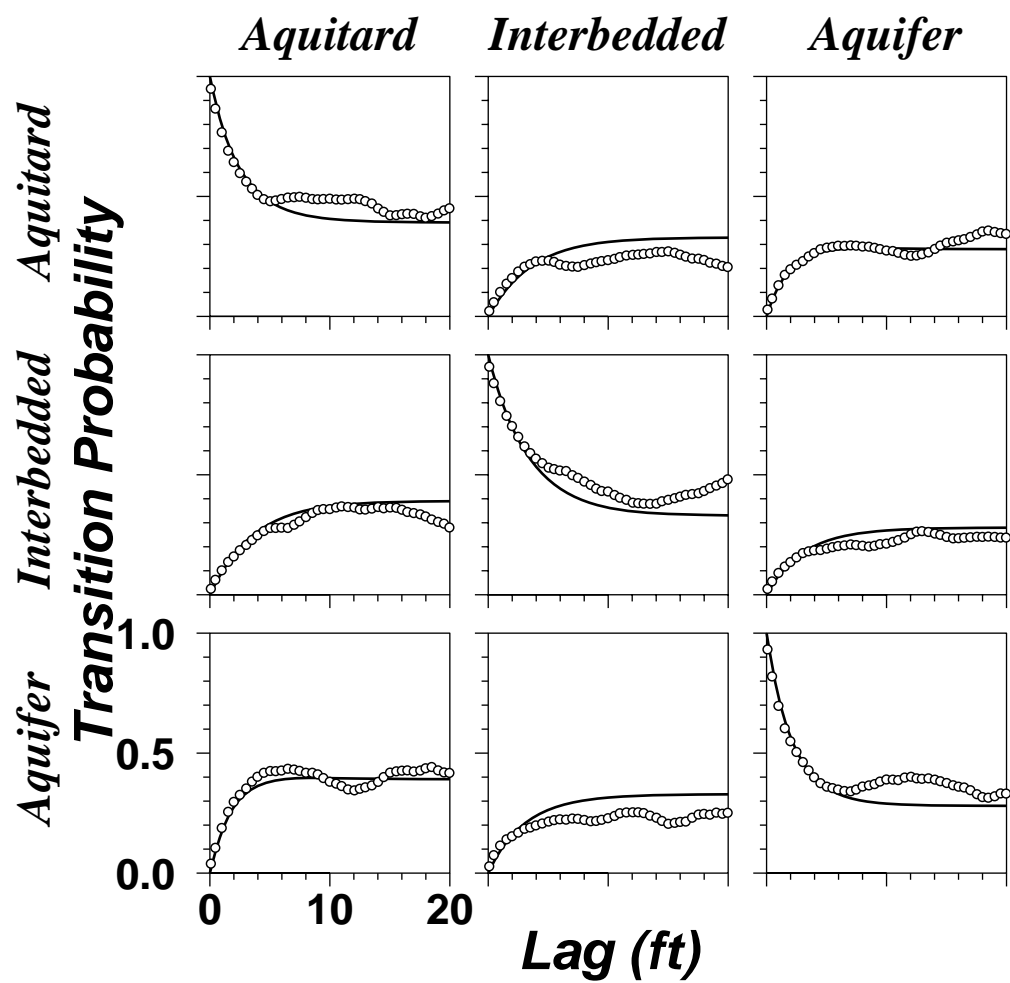


Figure 4. Geostatistical realization of hydrofacies architecture for Llagas subbasin.



Measured

○ ○ ○ ○ ○ ○ ○ ○

Markov Chain

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Figure 5. Vertical-direction hydrofacies transition probability measurements and Markov chain model.

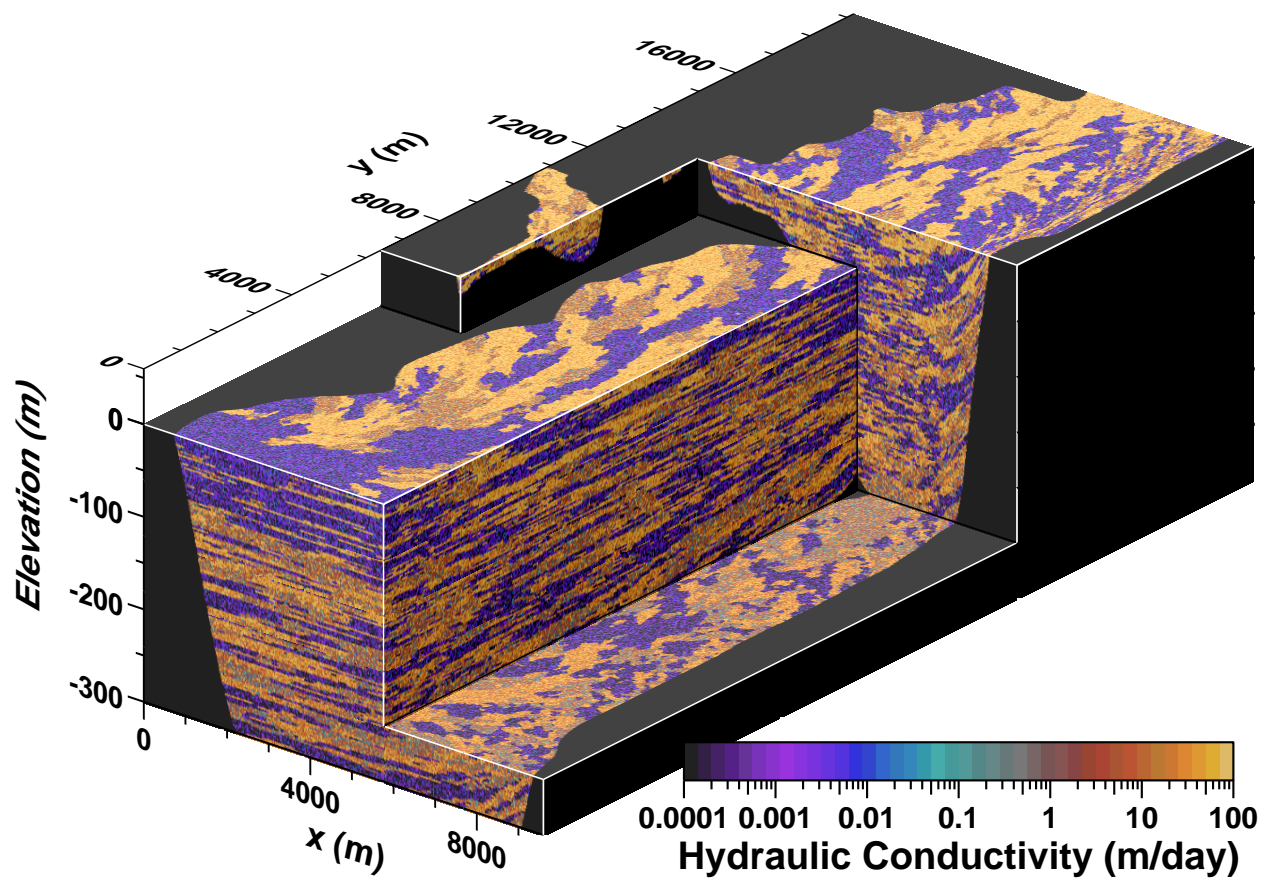


Figure 6. Geostatistical realization of hydraulic conductivity for Llagas subbasin.

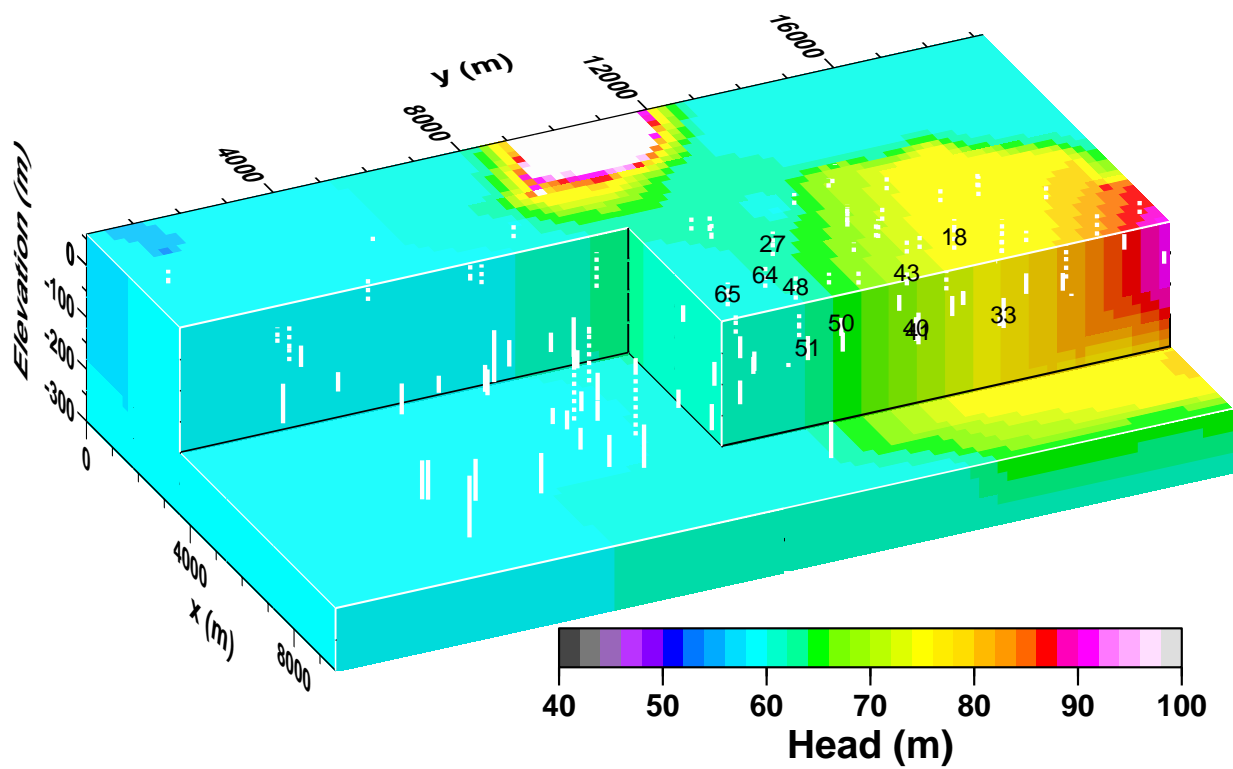


Figure 7. Simulated hydraulic head and pumping well locations for homogeneous model.

Numbered well locations indicate wells where significant nitrate breakthrough is simulated.

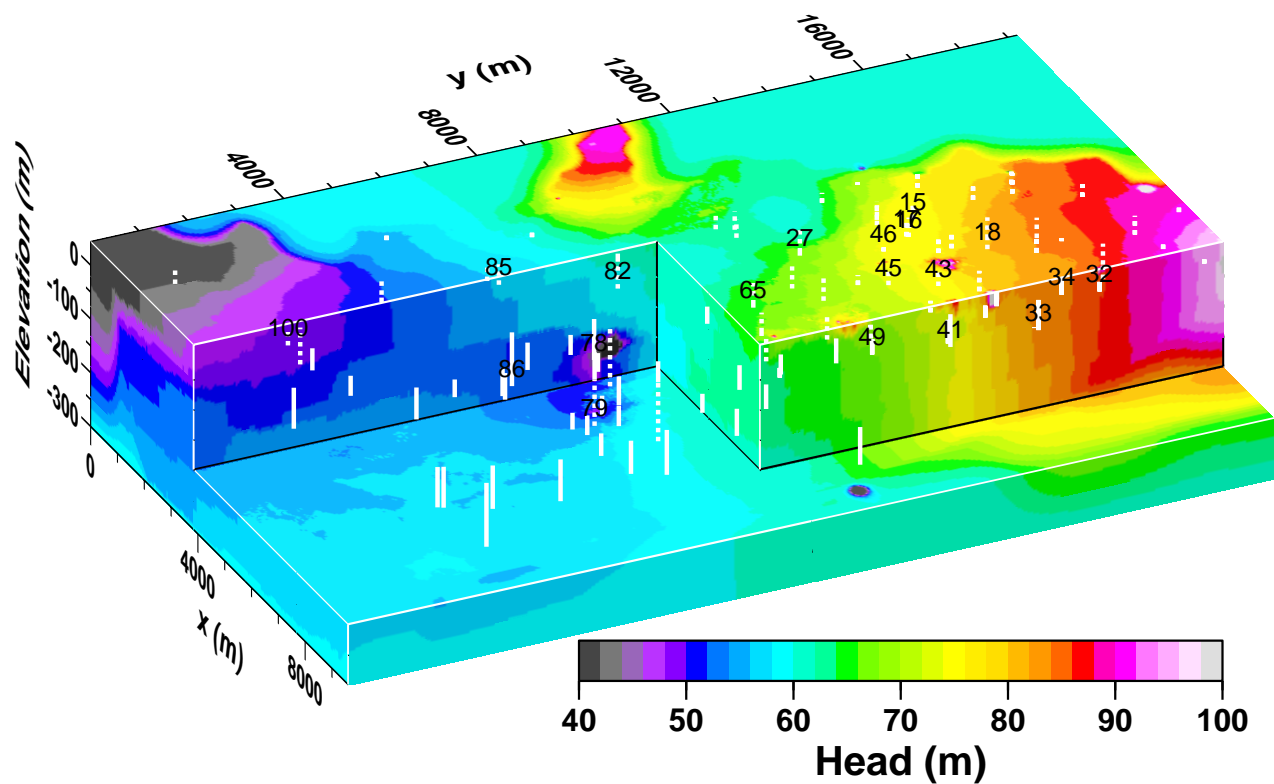


Figure 8. Simulated hydraulic head and pumping well locations for heterogeneous model.

Numbered well locations indicate wells where significant nitrate breakthrough is simulated.

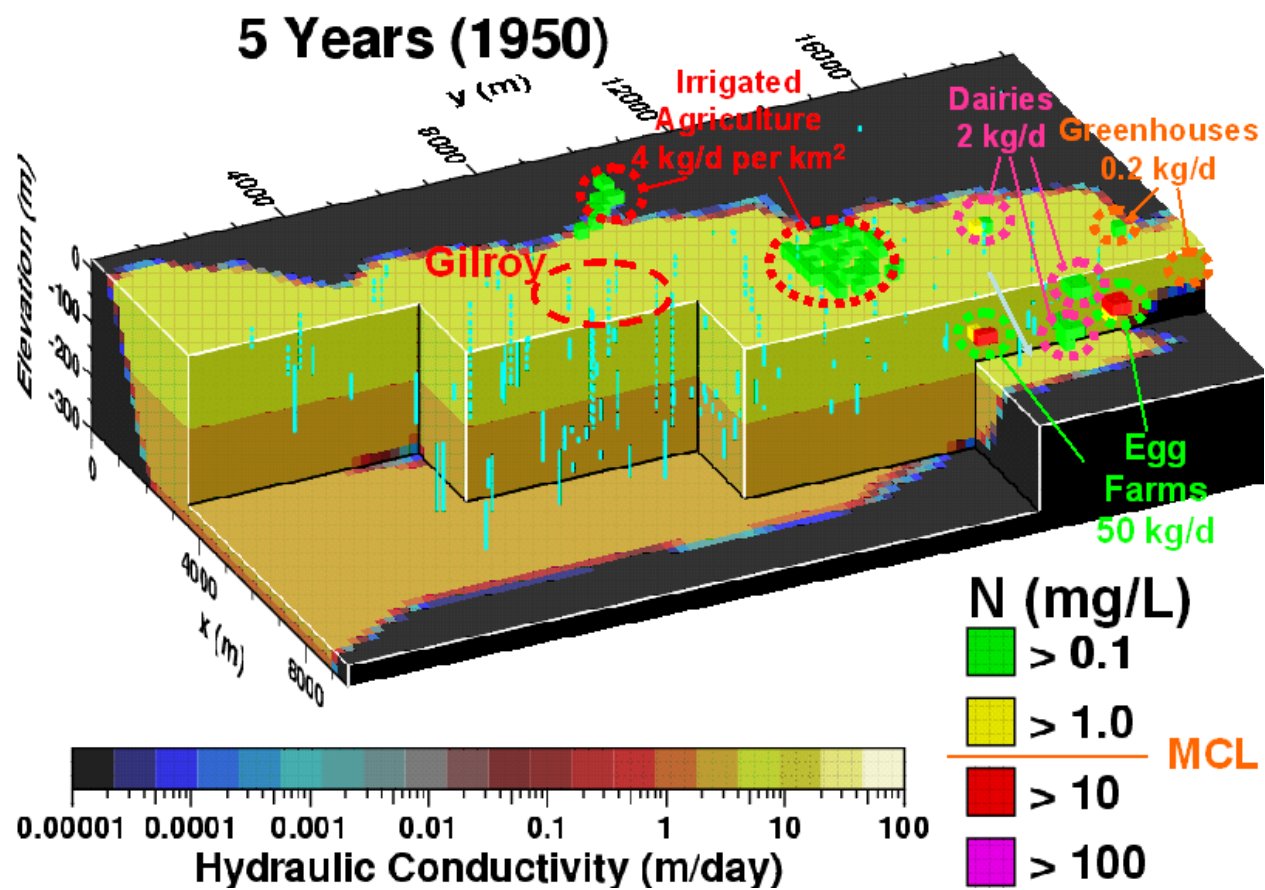


Figure 9. Locations of hypothetical nitrate loading sources for simulation.

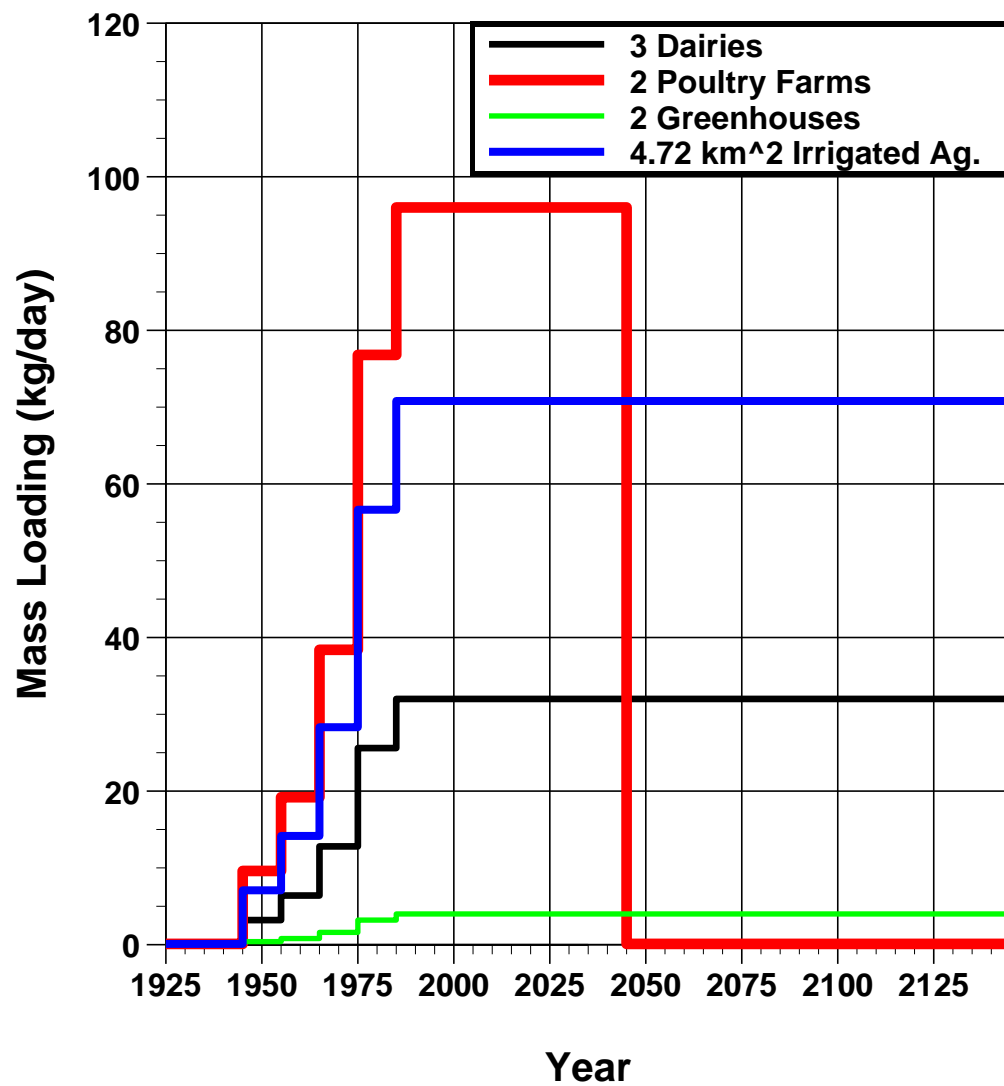


Figure 10. Nitrate loading source functions over time.

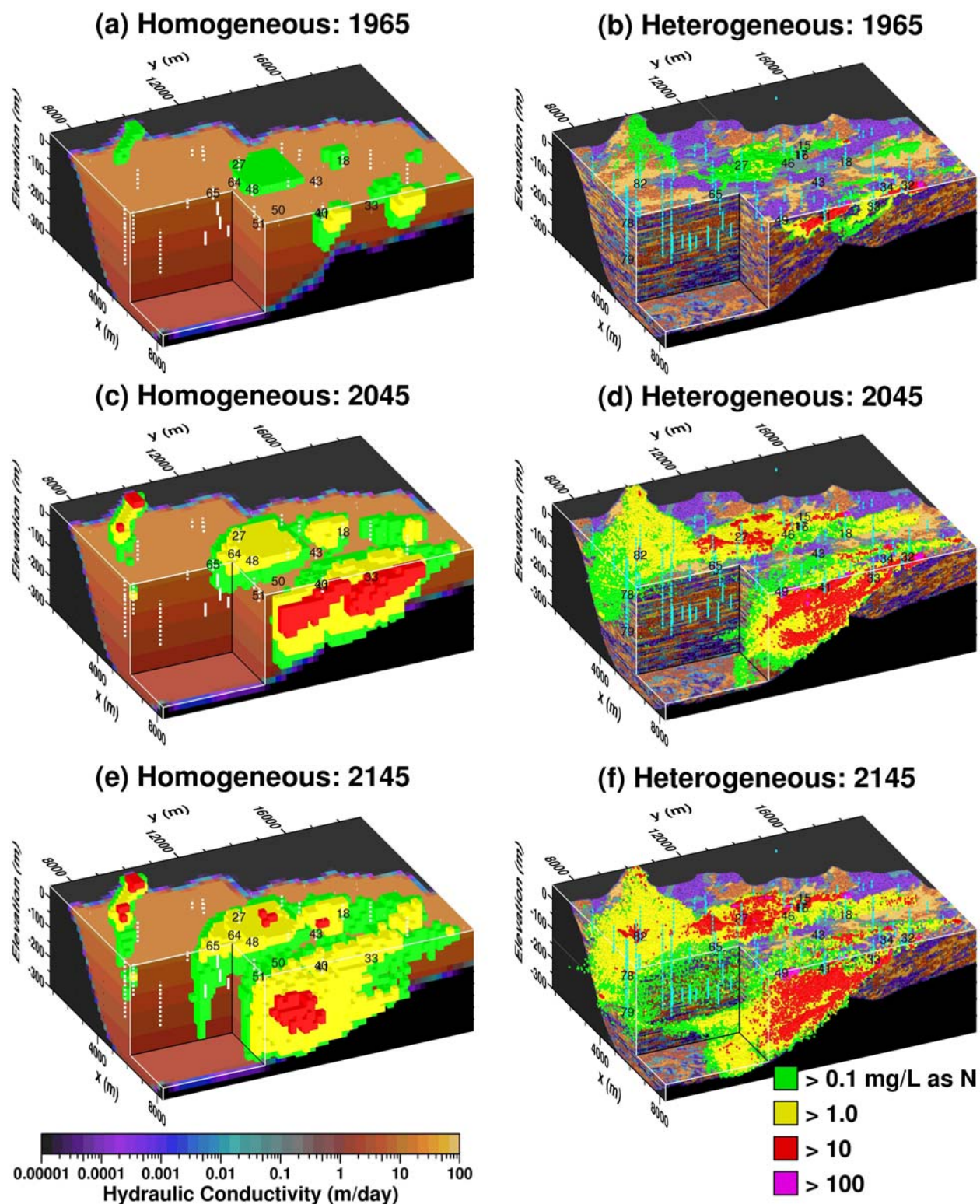


Figure 11. Three-dimensional view of simulated nitrate concentrations at years 1965, 2045, and 2145 (20, 100, and 200 yr since assumed beginning of nitrate loading).

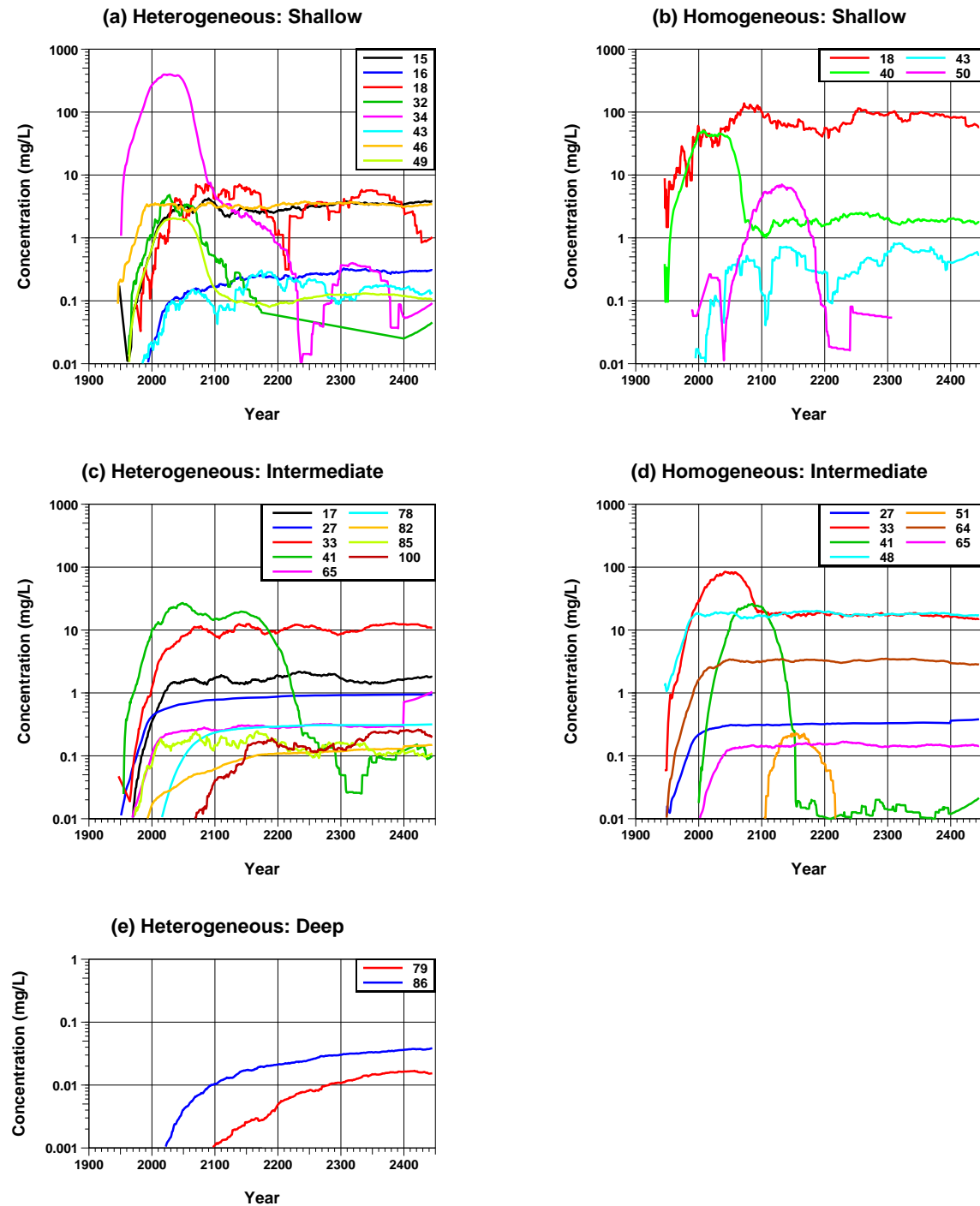


Figure 12. Simulated nitrate breakthrough curves (of anthropogenic nitrate concentration against time) for wells that exhibit peak anthropogenic nitrate concentrations of greater than 0.1 mg/L as nitrate.

Table 1: Hydraulic properties assigned to hydrofacies.

Hydrofacies	Porosity	Mean K (m/day)	Std. Dev. $\text{Log}_{10}(K)$
Aquitard	0.3	0.001	1.0
Interbedded	0.3	1.0	1.0
Aquifer	0.3	100.0	1.0

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Sources of groundwater nitrate revealed using residence time and isotope methods

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Sources of Groundwater Nitrate Revealed Using Residence Time and Isotope Methods

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Nitrate concentrations approaching and greater than the maximum contaminant level (MCL) are impairing the viability of many groundwater basins as drinking water sources. Nitrate isotope data are effective in determining contaminant sources, especially when combined with other isotopic tracers such as stable isotopes of water and tritium-helium ages to give insight into the routes and timing of nitrate inputs to the flow system. This combination of techniques is demonstrated in Livermore, CA, where it is determined that low nitrate reclaimed wastewater predominates in the northwest, while two flowpaths with distinct nitrate sources originate in the southeast. Along the eastern flowpath, $\delta^{15}\text{N}$ values greater than 10‰ indicate that animal waste is the primary source. Diminishing concentrations over time suggest that contamination results from historical land use practices. The other flowpath begins in an area where rapid recharge, primarily of low-nitrate imported water (identified by stable isotopes of water and a tritium-helium

residence time of less than 1 year), mobilizes a significant local nitrate source, bringing groundwater concentrations up to $53 \text{ mg NO}_3 \text{ L}^{-1}$. In this area, artificial recharge of imported water via local arroyos increases the flux of nitrate to the regional aquifer. The low $\delta^{15}\text{N}$ value (3.1‰) in this location implicates synthetic fertilizer. In addition to these anthropogenic sources, natural nitrate background levels between 15 and $20 \text{ mg NO}_3 \text{ L}^{-1}$ are found in deep wells with residence times greater than 50 years.

INTRODUCTION

Nitrate contamination of groundwater is a growing concern for drinking water supplies in many areas in the United States. Between 1993 and 2000, the U.S. Geological Survey's National Water-Quality Assessment program found that 9% of domestic supply wells and 2% of public supply wells exceeded the Environmental Protection Agency's maximum contaminant level (MCL) for drinking water of $45 \text{ mg NO}_3 \text{ L}^{-1}$ (10 mg L^{-1} as N; Nolan *et al.*, 2002). The California Department of Health Services reports that nitrate is the most common contaminant found in state groundwater and presents a serious threat to the groundwater supply (California Department of Health Services, 2004). In many groundwater basins, urbanization has created a growing demand for drinking water, while long histories of agricultural activity have left aquifers potentially at risk from nitrate.

Water agencies and regulators can develop more effective management strategies when nitrate sources are well understood. Many past studies have used ^{15}N and ^{18}O in nitrate as tracers of the source and fate of contamination (Kendall and Aravena, 2000). This dual isotope technique is sometimes limited by the overlap of source isotope values

and by the variety of potential processes that affect nitrate (Aravena *et al.*, 1993; Mengis *et al.*, 2001). Successful studies of nitrate behavior and distribution must take into account the many environmental and historical factors that affect nitrate fate and transport (Böhlke and Denver, 1995).

Our purpose is to improve upon traditional nitrate investigation methods that often yield ambiguous interpretations. We apply an integrated analytical approach using multiple lines of evidence to resolve the manifold origins and pathways of nitrate contamination. This approach is demonstrated in Livermore, CA, a city that relies on groundwater for a significant portion of its drinking water, but where MCL exceedances have occurred at 6 of the 13 public supply wells in the contaminated portion of the basin. As in many regions where this approach may be beneficially applied, Livermore has a decades long history of varied nitrate inputs in a complex groundwater system.

Previous studies of Livermore's nitrate problem have estimated nitrate loading from various sources using literature ranges of potential nitrate inputs from these sources (Steinbergs and Wong, 1980; Raines, Melton, and Carella, Inc., 2002). These assessments consider only theoretical calculations of modern inputs and do not account for residual inputs or for the effects of hydrogeology. In our study, we incorporate these factors by interpreting nitrate isotope and concentration data in the context of local hydrogeology and land use history. We consider nitrate interactions along flowpaths and we analyze dissolved gases to determine whether saturated-zone denitrification has taken place. Additionally, other isotopic tracers such as stable isotopes of water and tritium-helium residence times give valuable insight into the routes and timing of various nitrate contributions to the flow system.

STUDY SITE

The Livermore Valley lies 60 km east of San Francisco in the Diablo Range (Figure 1). It has a semiarid climate with an average annual precipitation of around 45 cm (State of California, 1967), 80% of which falls between November and March (Rees, 1994). Natural flow in the two principal streams, Arroyo Mocho and Arroyo Las Positas (Figure 1), is mostly runoff from precipitation in the hills. Since 1962, natural flow has been supplemented with imported water brought from the Sacramento-San Joaquin River Delta through the South Bay Aqueduct (SBA). Although the ratio of artificial to natural recharge varies, imported water is generally dominant, making up approximately three quarters of total recharge along Arroyo Mocho in 2003 (Segura, 2004). Water in the basin is managed for conjunctive use of groundwater and surface water by Alameda County Flood Control and Water Conservation District, Zone 7 (Zone 7).

The Livermore Valley Basin has two primary water-bearing formations. The Livermore Formation is a Plio-Pleistocene bedded sandy gravel with thin aquitards of sandy clay. This is overlain by Holocene age alluvial fill deposits of varying thickness, ranging from less than 30 m thick at the eastern edge to up to 210 m thick in the west (Figure 1; State of California, 1967; Moran *et al.*, 2002). The water table is typically 3 to 15 m below the land surface. Water level contours from 2002 are shown in Figure 2. Both layers are water bearing with higher yields observed in the alluvial deposits (State of California, 1967; Sorenson *et al.*, 1984; Moran *et al.*, 2002). Vertical transport between the formations is thought to be limited to areas where the Livermore Formation is in contact with the overlying stream channel deposits along the arroyos. The aquifer is

unconfined in the east; to the west, a series of clay aquicludes confines the aquifers (State of California, 1967). Surface and subsurface flow within the Livermore Valley tends to be toward the longitudinal axis of the valley from the north and south, and then westward along the longitudinal axis. Surface water flows into Alameda Creek and out of the watershed, while subsurface flow is drawn towards the major municipal well fields in the western basins (State of California, 1967). Through Zone 7's management, water levels have remained relatively constant for the last twenty years, after a period of groundwater overdraft from the 1940's to the early 1970's. The main flowpath follows an alluvial channel up to 90 m deep (Figure 2; State of California, 1967).

LAND USE HISTORY

Multiple potential nitrate sources in the Livermore Valley from both past and present land uses make it an ideal setting for a multi-tracer geochemistry approach. Nitrate monitoring programs identified two locations of particular concern as possible origins of contamination. Around the Livermore Wastewater Reclamation Plant (LWRP), treated wastewater is used in irrigation. In the 1980s, contributions from LWRP were identified as the cause of high levels of nitrate in groundwater in that area (Sylvester, 1983). Subsequently, wastewater treatment methods were upgraded to include a tertiary treatment step that induces denitrification and reduces nutrient concentrations considerably. In 2003, the average monthly nitrate concentration in the applied water was only 4.9 mg L^{-1} (pers. comm., D. Atkins, LWRP).

The other area of concern is the unincorporated southeast region of the valley (Figure 1). Past monitoring data show that as early as 1980, a nitrate plume originating in

this location extended at least to the area where most groundwater extraction for drinking water takes place (Figure 1; unpublished data, Zone 7, 2003). A number of possible nitrate contamination sources exist in the southeast. Several reports in the past have implicated septic leachate as a primary nitrate source (Sylvester, 1983; Sorenson *et al.*, 1984; Raines, Melton, and Carella, Inc., 2002). In this unsewered area, approximately 100 residences have septic systems, a number that has not changed significantly in the past 30 years (Raines, Melton, and Carella, Inc., 2002). Another possible source is livestock waste from both modern and historical inputs. For many decades, ending in the early 1970s, poultry farming was a significant operation in this area. Over the last century, various grazing operations have existed on the grassland to the south and east of this area (Raines, Melton, and Carella, Inc., 2002).

This southeast region also includes vineyards which have increased in acreage over the last several decades to the current area of approximately 8 km² (Raines, Melton, and Carella, Inc., 2002). Although vineyards tend to use less nitrogen fertilizer than vegetable crops, they can still contribute significant nitrate to groundwater. One recent report found groundwater nitrate concentrations of up to 61.6 mg L⁻¹ beneath grape fields in the San Joaquin Valley, CA (Burow, *et al.*, 1998), while another demonstrated that, even with closely controlled drip irrigation, 67% to 79% of fertilizer nitrogen applied to vineyards in the spring remained in the soil at harvest time, available for leaching with winter rains (Hajrasuliha, 1998).

Another possible nitrate source in the valley is that formed from the oxidation of organic nitrogen, naturally found in soil as a result of plant decomposition and microbial activity (Kendall and Aravena, 2000). Natural nitrate concentrations in groundwater

below temperate region grasslands, unimpacted by anthropogenic activities, are generally below 9 mg L⁻¹ (Edmunds and Gaye, 1997). In arid and semiarid regions where denitrification is unlikely, however, greater amounts of natural nitrate can accumulate in soils and be available for leaching to groundwater (Edmunds and Gaye, 1997; Brenner *et al.*, 2001; Böhlke, 2002). In Livermore's climate and habitat, leguminous vegetation that supports nitrogen-fixing bacteria is an important potential nitrate source. Burr clover and vetch, species that produce between 90 and 200 kg ha⁻¹ y⁻¹ of nitrate (National Research Council, 1993), thrive in Livermore during warm, wet winters (Steinbergs and Wong, 1980). It is often assumed that nitrate produced by legumes is balanced by denitrification (Steinbergs and Wong, 1980), but in Livermore's dry summer season, it is possible that there is not enough soil moisture to support denitrification of this large quantity of nitrate. A study in a North African region with a similar semiarid climate attributed groundwater nitrate levels as high as 250 mg L⁻¹ to nitrogen fixed by legumes (Edmunds and Gaye, 1997).

METHODS

Sample Collection

The thirty-three well sampling locations from 2003 are shown in Figure 2 and described in Table 1. At monitoring wells, samples were taken using a portable submersible pump. At other wells, dedicated well pumps were used. Most ion and isotope samples were filtered in the field with a 0.45µm in-line filter. Nitrate isotope samples were loaded onto anion exchange columns within 24 hours of sampling, and ion analyses were performed within 48 hours of sampling. For dissolved gas analyses of

nitrogen, oxygen, and argon, samples were collected in 40-mL vials (VWR TraceCleanTM, amber borosilicate; 0.125-inch septum liner) with no headspace. Samples were stored in coolers on ice and analyzed on the same day as sampled. A 1-L Pyrex bottle with a polypropylene plug seal cap was filled for tritium analysis and a 30-mL clear, French-square type glass bottle with a QorpakTM polyseal-lined cap was filled for analysis of stable isotopes of water. Approximately 10 mL were collected in copper tubes pinched by metal clamps for noble gas samples.

Total organic carbon (TOC) samples and field dissolved oxygen (DO) data were collected at these wells in 2000. TOC samples were collected in 150 mL amber borosilicate glass, preserved with concentrated HCl, and refrigerated until analysis. Field DO was measured using a Horiba U-22 multi-parameter water quality probe with a flow-through cell. Uncertainty in DO measurement is ± 0.3 mg/L.

Laboratory Methods

Nitrate isotope samples were analyzed at the Environmental Isotopes Lab at the University of Waterloo. After extraction as silver nitrate (Silva *et al.*, 2000), nitrogen gas for the measurement of $\delta^{15}\text{N}$ was produced by the sealed tube Cu/copper oxide method (Kendall and Grim, 1990) and CO_2 for measurement of $\delta^{18}\text{O}$ was produced by combustion with graphite. The isotope ratios of these gases were measured on a PRISM isotope ratio mass spectrometer (Flatt and Heemskerk, 1997). $\delta^{15}\text{N}$ results are reported as per mil relative to AIR and $\delta^{18}\text{O}$ results are referenced to VSMOW. The noble gases ^3He , ^4He , Ne, Ar, Kr, and Xe were measured at Lawrence Livermore National Laboratory (LLNL). ^3He and ^4He were measured on a VG5400 mass spectrometer, Ar was measured using a high-sensitivity capacitive manometer, and Ne, Kr, and Xe were measured on a

quadropole mass spectrometer (Bayer *et al.*, 1989; Beyerle *et al.*, 2000). Tritium was determined by measuring the rate of ^3He accumulation after degassing the sample under vacuum (Eaton *et al.*, 2003). Anions and cations were measured by ion chromatography at LLNL on a Dionex IC DX-600 with a precision of $\pm 2.7\%$ relative standard deviation for nitrate. Oxygen isotopes of water were measured at LLNL using the CO_2 equilibration method (Epstein and Mayeda, 1953), with isotope ratio measurements made on a VG PRISM isotope ratio mass spectrometer. Results are reported as per mil with reference to VSMOW and have a precision of $\pm 0.1\%$. Deuterium was measured at the University of Arizona using a Finnigan Delta S isotope ratio mass spectrometer. Samples were first reacted with Cr at 750 C in a Finnigan H/Device coupled to the mass spectrometer. Results are reported as per mil with reference to VSMOW and have a precision of $\pm 0.9\%$. Dissolved nitrogen and argon gases for examination of excess nitrogen were measured at LLNL by membrane inlet mass spectrometry (MIMS) with an SRS RGA200 quadropole mass spectrometer (Kana *et al.*, 1994). TOC was measured using an OI Corporation Model 1010 wet chemical oxidation TIC-TOC analyzer at LLNL. The analytical uncertainty is less than or equal to 0.3 mg/L.

Isotope and Dissolved Gas Techniques

A variety of nitrate fractionation processes lead to distinctive isotopic signatures for different nitrate sources. As a result, isotope values of nitrogen and oxygen can be useful in identifying the origin of groundwater nitrate. Synthetic fertilizers generally have $\delta^{15}\text{N}$ values between -2% and $+4\%$ (Kendall and Aravena, 2000). By the time it reaches the groundwater, however, fertilizer nitrogen tends to be enriched by several per mil over the original source, often making it indistinguishable from soil organic nitrogen,

which tends to have $\delta^{15}\text{N}$ values of +3‰ to +8‰ (Brenner, 2001; Karr *et al.*, 2001; Choi *et al.*, 2003). Nitrate from animal waste has higher $\delta^{15}\text{N}$ values, usually greater than +10‰, and so can often be distinguished from other sources. All animals produce waste with similar $\delta^{15}\text{N}$ values, though, so isotopes alone are usually not useful in differentiating between human waste and other animal wastes (Kendall and Aravena, 2000).

Oxygen isotope values of nitrate can help clarify source identification, especially to separate nitrate fertilizer input from other sources, which produce nitrate by nitrification of ammonium or organic nitrogen. Nitrate in synthetic fertilizers is derived from atmospheric nitrogen and so is expected to have a $\delta^{18}\text{O}$ value close to the atmospheric value of +23.5‰. Nitrate from other sources tends to have lighter $\delta^{18}\text{O}$ values because the nitrification process incorporates only one oxygen from dissolved atmospheric oxygen and the other two from water (Kendall and Aravena, 2000). Nitrate from ammonium nitrate fertilizers will have $\delta^{18}\text{O}$ values that reflect both processes (Aravena *et al.*, 1993).

Denitrification produces signatures both in the nitrate isotopes and dissolved gas ratios. As denitrification occurs, nitrogen and oxygen isotopes in nitrate from freshwater are typically enriched in a characteristic pattern with a ratio close to 2:1 (Kendall and Aravena, 2000). Saturated zone denitrification can also be identified by the presence of its end product, nitrogen gas dissolved in groundwater in excess of that expected from equilibration with the atmosphere (“excess N_2 ”). Comparison with dissolved argon distinguishes this excess N_2 from the two sources of atmospheric nitrogen, either nitrogen dissolved (1) through equilibration with air, or (2) from excess air, which is the product

of air bubbles dissolved under pressure. A nitrogen to argon equilibrium solubility ratio can be predicted based on the recharge temperature derived from noble gas data. A trend of potential nitrogen to argon ratios that incorporate excess air can be extended from this initial equilibrium solubility point (Figure 3). A nitrogen to argon ratio that deviated from this excess air trend towards higher nitrogen would indicate excess N₂ was present and that denitrification had occurred. Only saturated zone denitrification can be detected using this technique; in the unsaturated zone, the nitrogen gas produced may be lost to the atmosphere or diluted by the large pool of atmospheric nitrogen present there (Vogel *et al.*, 1981; Böhlke and Denver, 1995).

Mean groundwater residence time is calculated using the tritium-helium method. Tritiogenic helium is calculated after correcting for other helium sources: noble gas concentrations and solubility trends define the recharge temperature and allow for estimation of the atmospheric and excess air helium components. These calculations were made assuming complete dissolution of excess air, an assumption that may lead to slight error in the calculated recharge temperature (Aeschbach-Hertig, *et al.*, 2000). Radiogenic ³He produced through sediment U and Th decay is assumed to have a typical ³He/⁴He ratio of 2×10^{-8} (Solomon and Cook, 2000; Hudson *et al.*, 2002). These shallow wells show no evidence of the presence of mantle or significant crustal radiogenic helium. The remaining ³He is the result of tritium decay and, along with measured tritium and tritium's known half-life (12.32 y; Lucas and Unterwerger, 2000), can be used to determine the mean time since recharge for the mixture of water in a sample (Schlosser *et al.*, 1989; Solomon and Cook, 2000; Hudson *et al.*, 2002). Groundwater in areas with low recharge can lose tritiogenic ³He through diffusion across the water table

(Schlosser, 1989), a concern in semi-arid areas like Livermore. In these calculations, we assume that the recharge rate is high enough to limit ^3He loss. This assumption is generally justified by the local high rates of artificial recharge but may lead to some underestimation of residence time. The calculated residence times can be most confidently interpreted as representing the time since recharged water remained several meters or more below the soil-water interface. A 'younger' mean residence time represents a higher fraction of recently recharged water. Tritium-free water recharged more than about 50 years ago.

RESULTS AND DISCUSSION

Nitrate-source data is most successfully interpreted in the context of the constraints that can be placed on the groundwater flow system using conventional hydrogeological data along with other isotopic and geochemical tracers. Nitrate concentrations are highest in the southeast part of the study area, where many of the wells exceed the MCL (Table 1). The contamination extends to the area of major groundwater extraction as shown in the contour map in Figure 1. In conjunction with the estimated flowpaths, this supports the conclusion of past studies that the most significant nitrate contamination originates in the southeastern recharge area. Current and historical data consistently record higher nitrate concentrations in shallow monitoring wells than in deep wells, suggesting a plume with a shallow core. Nitrate concentrations identify the problem regions but are not diagnostic for distinguishing among competing sources or for helping identify historic or contemporary land use practice culpability. The following

methods illustrate how critical additional insights are gained with each additional isotope and dissolved gas measurement.

Excess Nitrogen

The possibility of saturated zone denitrification must be considered before any conclusions can be drawn based on nitrate concentrations or nitrate isotope values. Samples for which noble gas data are available have recharge temperatures calculated to be between 11 and 22 C (Table 1). Nearly all nitrogen to argon ratios fall within the general range delineated for these temperatures by equilibrium solubilities and excess air trends, indicating that excess N₂ is not present. Although these results do not exclude the possibility of denitrification before transport to the water table, they demonstrate that saturated zone denitrification is not an important process. This result is consistent with low dissolved organic carbon and high dissolved oxygen measurements that indicate an aerobic system with low reduction potential and lack of an electron donor. Groundwater nitrate data, therefore, may be interpreted directly as indicative of nitrate source, without accounting for attenuation or isotopic enrichment due to denitrification along the flowpath.

Groundwater Sources

We use stable isotopes of water to establish groundwater provenance (Figure 4). The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ 2003 groundwater data fit into a trendline falling slightly below the Global Meteoric Water Line (Rozanski, 1993) with a slope generally parallel to it, suggestive of a local meteoric water line trend. The nearest station for which long term precipitation data have been collected is in Santa Maria, CA 400 km to the south (GNIP, 2004). The Livermore well data fall within the general range defined by Santa Maria

precipitation isotopes, although the Livermore groundwater's $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are somewhat lighter due to its higher elevation and inland location. Adherence to a LMWL without significant deviation provides evidence that this groundwater experienced little evaporation prior to recharge.

These isotopic data are also useful in distinguishing between the three most probable sources of water to the aquifer: modern precipitation, imported South Bay Aqueduct (SBA) water, and ambient groundwater old enough to predate California's history of large-scale water manipulation (Figure 4). Originating mostly at higher elevations in the Sierra Nevada Mountains, SBA water is isotopically lighter than local precipitation. SBA water recharges the aquifer along Arroyo Mocho from April to November and also makes up 95% of irrigation water and approximately 80% of domestic water in the area (Segura, 2004). Older ambient groundwater, identified by its lack of tritium, appears at the heavier end of the observed trend. The various mixing fractions of the three possible sources of water are evident in the isotope data, but the large range observed in local precipitation (-14.8 to -0.3‰ $\delta^{18}\text{O}$; pers. comm., T. Rose, LLNL) prevents quantitative determination of the three fractions. In general, local precipitation is a dominant source, and the shallow and proximal wells to Arroyo Mocho (i.e. wells 22B1, 16E4) contain higher fractions of SBA water, while deeper wells (i.e. wells 10Q2, 7P3) have high fractions of older groundwater.

The groundwater flow system can be further constrained by defining the recharge area using tritium-helium residence time data, with the youngest ages representing locations of most recent recharge (Table 1). The shallow wells nearest the arroyo have residence times of less than one year, and other shallow wells have residence times of

less than ten years. These data suggest diffuse recharge throughout the study area with substantial recharge and relatively rapid groundwater flow along the arroyo. Along the coarse sediments of the alluvial channel, there is a general correlation between mid-screen well depth and groundwater mean residence time. Even the deepest alluvial channel well (well 9Q1) has a significantly higher fraction of young water than the tritium-free deep western wells that are protected by a series of clay layers (wells 7P3 and 7R3). The primary sources of modern recharge, SBA water and precipitation, are both very low in nitrate and cannot be directly implicated as nitrate sources (State of California, 2004).

Groundwater Chemistry

Measurement of additional ion concentrations allows for separation of the nitrate plume into well-defined spatial groups based on differing solute composition. A plot of chloride vs. sulfate shows that data from 71% of the wells lie along a constant ratio trend, indicating the similarity of water type and ion source in these wells (Figure 5). This main trend includes the wells along the Alluvial Channel Flowpath and south to Arroyo Mocho. A relatively high chloride to sulfate ratio separates two Boundary Flowpath wells, wells 10Q1 and 15J2, from the rest of the wells in that region, which follow the main trend. Ion data from wells around the LWRP wastewater application area form a distinct lower slope trend, establishing that these wells are dominated by a different water source than the rest of the study area. The low ion end member of this LWRP trend is defined by the area's deeper, confined wells. These wells have a chloride to sulfate ratio matching that of the main trend, suggesting that the water source impacting the shallow wells does not reach the lower aquifers. Well 22B1 stands out due to its high sulfate

levels. After remaining relatively steady for more than 20 years, sulfate concentrations in well 22B1 began rising in 1999, reaching 190 mg L⁻¹ in 2003, nearly four times the earlier level (unpublished data, Zone 7, 2003). Calcium concentrations showed a significant increase at about the same time, suggesting a major land use change, perhaps a change in vineyard fertilization or soil amendment application.

Nitrate Sources

Applied Wastewater

In the northwest region around the LWRP, nitrate isotope data confirm that the shallow wells here have a different nitrate source than in the rest of the study area (Figure 6). Shallow nitrate- $\delta^{15}\text{N}$ values are between 13.0‰ and 29.2‰, in the range expected for treated wastewater effluent (Jordan *et al.*, 1997; Griggs *et al.*, 2003). The nitrate- $\delta^{18}\text{O}$ values are the highest of all measured samples, consistent with the expected fractionation effects of denitrification, induced by LWRP as a wastewater processing technique. These data signify that irrigation with reclaimed wastewater is the source of this area's distinctive geochemical signature. Water in the deeper wells, unimpacted by irrigation, has nitrate- $\delta^{15}\text{N}$ values (6.7‰ to 8.8‰) comparable to the other main trend wells. Stable isotopes of water provide further evidence that the confining layers have prevented applied wastewater from reaching the deeper aquifers; water from these aquifers has an isotopic signature suggesting a precipitation source, while samples from the unconfined layer have heavier $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, likely the result of fractionation during wastewater processing.

Although this LWRP region was identified as a high nitrate source area in the past (Sylvester, 1983), most of the wells currently have nitrate concentrations well below the

MCL (Table 1). The one well within the area of wastewater application for which long term historical data are available, well 2R1, shows concentrations as high as 75 mg L⁻¹ in the late 1970s. After modernization of treatment facilities in 1981, nitrate levels began to drop, reaching concentrations around 10 mg L⁻¹ in the space of just five years. This demonstrates that the new wastewater treatment methods have been successful at reducing nitrogen loading to the aquifer from reclaimed water irrigation.

Manure

The southeastern region has been identified as the starting point of the high concentration plume. Although the potential nitrate contamination sources are the same for all of the wells in this area, the ionic composition of wells 15J2 and 10Q1 stands out from the rest (Figure 5). The more northerly Boundary Flowpath on which these wells lie is likely impacted by a different primary nitrate source than the rest of the valley (Figure 2). Measured nitrate- $\delta^{15}\text{N}$ values greater than 10‰ identify animal or human waste as the nitrate source in these wells, but these isotope data do not distinguish between these two inputs. Examining observed historical trends provides further insight. Time series reconstructions of past nitrate concentrations at these wells show that both have had a trend of significantly decreasing nitrate concentrations for at least twenty years (Figure 7). Current nitrate concentrations at both wells are less than a third of peak values and are nearly at the MCL. Although some modern nitrate sources may remain, it seems that a major source has been discontinued or significantly diminished. Because septic and fertilizer input in this area have remained steady or have increased over the last few decades, historical livestock waste (most active inputs approximately 1950 to 1975) is implicated as a major contributor to nitrate contamination along this flowpath.

Tritium-helium mean residence times of 4 and 9 years in wells 10Q1 and 15J2 demonstrate rapid recharge in this manure-impacted area. As discussed above, however, the contamination in this water comes from sources that were present at the land surface decades ago. This describes a situation in which historical contamination stored in the vadose zone is being flushed into the groundwater over time. This rapid flow and historically-sourced nitrate contamination affects only the shallow part of the aquifer; well 10Q2, 80 m deeper than well 10Q1, had a nitrate concentration of 16.2 mg L^{-1} , compared to 60.2 mg L^{-1} in the shallow well. No tritium was detected in well 10Q2, indicating that water at this depth is greater than 50 years old. The sum of the evidence therefore suggests limited vertical flow and little interaction between the upper and lower aquifers in this area of thin alluvial fill.

Fertilizer and Soil Organic Nitrogen

To supplement nitrate-source information provided by nitrate concentration and isotope data, historical ion data combined with residence time measurements yield critical information regarding the impacts of natural background processes versus the impacts of past or present anthropogenic processes. It is constructive to consider data grouped by the depth of the wells and the hydrogeological layers they tap rather than by geographic location alone. The main trend identified by the anion data, which covers a wide area where diffuse recharge and discharge (pumping) complicate the flow system, is considered as two groups (Figures 2, 5). In one group, wells either pump from aquifers confined beneath several aquicludes or else are predominantly screened at depths greater than 80 m. Three deep wells with tritium concentrations of less than 1 pCi/L (wells 7P3, 7R3, and 10Q2) provide an archive of groundwater that recharged before major inputs of

non-natural nitrate. At these wells, groundwater is not impacted significantly by the shallow zone contamination, suggesting that the nitrate detected here represents a natural background. Yet nitrate concentrations in these wells are between 15 mg L⁻¹ and 20 mg L⁻¹, which is higher than generally expected for nitrate from non-anthropogenic sources (Nolan, 2002). As discussed above, this result can be explained by nitrogen-fixing vegetation in Livermore's semi-arid climate. Nitrate- $\delta^{15}\text{N}$ values between 6.3‰ and 7.6‰ support the hypothesis of soil organic nitrogen as a natural nitrate source. Other deep wells produce groundwater that is a mixture of tritiated water with high nitrate values and water recharged more than 50 years ago, which likely dilutes the nitrate concentration to some extent. Deeper penetration of younger water in these wells is the result of the influence of pumping patterns and of location with respect to the arroyo and to overlying alluvial fill.

The rest of the samples fitting the main anion trend are found in wells that draw primarily from the top alluvial layer. This group includes all wells along the flowpath following the central alluvial channel plus the shallow wells between this channel and Arroyo Mocho (Figure 2). The Alluvial Channel Flowpath follows roughly the same course as the nitrate plume originating in the southeast. In contrast to the Boundary Flowpath that also originates in that area, nitrate concentrations in wells along the alluvial channel have been steady or rising throughout the last few decades. Well 9Q4 is representative of the alluvial channel wells in the shallow zone of the aquifer. Nitrate levels there averaged around 65 mg L⁻¹ for two decades until a moderate decline was observed over the last five years (Figure 7). In the deeper alluvial channel wells, nitrate levels have been increasing slowly, so that even the deepest well (9Q1) has recently

surpassed the MCL (Figure 7). This supports the depiction of a separate nitrate source along this flowpath and suggests a source with continuing input rather than a historical source.

Well 22B1 is particularly useful in providing the chemical and isotopic signature of the contaminated alluvial channel end-member, since it is situated at the head of the source area, has a high nitrate concentration, and produces very recently recharged groundwater. This well is at the southeastern perimeter of the nitrate contamination plume and adjacent to Arroyo Mocho (Figure 2). Multi-tracer data reveal unusual conditions in this area that provide important insight into the origin of the contamination. Well 16E4 is another shallow well adjacent to the arroyo but several km to the west of well 22B1. Light stable isotopes of water at both wells indicate that they draw the majority of their water from recharge of SBA water along the arroyo (Table 1). Tritium-helium residence times of less than one year at both wells also indicate that rapid recharge from the arroyo is a significant source of shallow groundwater proximal to the arroyo. These wells experience high recharge from the nearby arroyo, in which flow is maintained year round. Potential error in the calculated residence time due to ^3He diffusion loss is therefore minimal. Despite this evidence that these two wells have the same source of water, their observed nitrate concentrations are very different. Well 16E4 generally has less than $10 \text{ mg L}^{-1} \text{ NO}_3$ while well 22B1 historically fluctuates between 30 mg L^{-1} and $80 \text{ mg L}^{-1} \text{ NO}_3$ (unpublished data, Zone 7, 2003). SBA water contributes little nitrate, with an average concentration over the last 10 years of 2.5 mg L^{-1} (State of California, 2004). To reach the high nitrate levels seen at 22B1, then, recharge through the arroyo must mobilize a local source of nitrate in its short travel time to the well. This

represents a substantial amount of nitrogen moving through the system, and must either be supplied by a large reserve stored in the soil or vadose zone or by a source that is continually being replenished. Either a soil or fertilizer source, therefore, is implicated as the source of nitrate in this location.

All nitrate concentrations measured in the alluvial region were greater than 33 mg L⁻¹ and $\delta^{15}\text{N}$ values were less than 8‰ (Figure 6). Well 22B1 and well 15G4 have high nitrate concentrations, 53.1 and 53.8 mg L⁻¹, and are in the high end of the isotope range expected for synthetic fertilizer (3.1‰ and 4.8‰ nitrate- $\delta^{15}\text{N}$ values, respectively). This also overlaps the low end of the range for nitrate from reduced soil nitrogen, another potential source given these wells' location downgradient of vineyards and grassland. Although nitrogen isotopes alone cannot distinguish between these two sources, it is unlikely that concentrations as high as 80 mg L⁻¹, which have been measured at well 22B1, result from soil nitrogen inputs alone. As groundwater flows from the southeast to the northwest along the Alluvial Channel Flowpath, the trend, originating at well 22B1, is towards decreasing nitrate concentrations and increasing $\delta^{15}\text{N}$ values (Figure 6). In the absence of denitrification, remineralizing nitrate in the soil and mixing with uncontaminated water would result in such a trend toward decreased nitrate concentrations and increasing nitrate- $\delta^{15}\text{N}$ values into the range expected for soil nitrogen (Choi, 2003).

Nitrate- $\delta^{18}\text{O}$ data provide further evidence for a fertilizer source of nitrate in this area. Wells 22B1, 15G4, and 15G5 have nitrate- $\delta^{18}\text{O}$ values between 8.1‰ and 10.9‰ (Table 1), relatively high compared to the values found at the other shallow wells with low $\delta^{15}\text{N}$, which range from 2.8‰ to 4.8‰ nitrate- $\delta^{18}\text{O}$. High nitrate- $\delta^{18}\text{O}$ is consistent

with a synthetic fertilizer nitrate source. Nitrate from synthetic fertilizer generally has a nitrate- $\delta^{18}\text{O}$ value around 23‰ (Kendall and Aravena, 2000), while ammonium nitrate fertilizer, with approximately 50% of its oxygen from fertilizer nitrate and 50% from nitrified fertilizer ammonium, would be expected to have a nitrate- $\delta^{18}\text{O}$ value of approximately 13‰ in this environment (Aravena *et al.*, 1993).

CONCLUSIONS

In this study, the separation of nitrate sources introduced decades ago is made possible by a multiple-analysis approach using current and historical data. Stable isotopes provide information about water sources, while tritium-helium age dating defines groundwater residence times and transport behavior. In addition, dissolved gas and nitrate isotope evidence indicate that nitrate moves conservatively in the groundwater, which simplifies source attribution. Nitrate isotope measurements are then combined with information about land use history to identify contaminant sources. Based on this data, several flowpaths originating in the southeastern region were identified, one primarily impacted by historical manure sources and the other with a significant modern synthetic fertilizer component. This integrated approach reveals a much larger role for fertilizer and natural soil nitrogen than suggested by prior assessments, which used source mass and plume delineation methods to attribute most of the contamination to septic tanks and livestock. In addition to identifying contaminant sources, these methods offer a deeper understanding of how the severity and extent of contamination is affected by hydrogeology and groundwater management practices. In this case, the nitrate problem is amplified by artificial recharge in the source area, a

region where the aquifer is vulnerable because it is unconfined and experiences high vertical recharge. This approach can be widely applied to other regions with historical nitrate inputs and can provide valuable information to water managers in evaluating future mitigation strategies.

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FIGURES AND TABLES

Figure 1. Nitrate concentrations in Livermore Valley. Approximate nitrate contours, in mg/L, kriged using RockWareTM. Based on previous dataset from 2000 except for two points from 2001, included to more accurately delineate the boundary of the contaminated region. All wells have depths less than 35 m, the approximate depth of a non-continuous aquiclude and thus the defined cutoff for the aquifer's shallow zone. The apparent gap in the central valley is an artifact of the limitations of the data, rather than a break in the plume.

Figure 2. 2003 sampling locations. Symbols represent spatial groups referred to in Figures 3 through 5. Main flowpaths, estimated from 2002 water level measurements (shown in inset in meters above mean sea level; C. Winey, Zone 7, pers. comm.), are illustrated with arrows.

Figure 3. Dissolved nitrogen versus dissolved argon. The WEA ("water equilibrated with air") line represents the nitrogen and argon ratio expected based on equilibrium solubilities of the gases. The excess air lines are projected by assuming that excess air is the result of complete dissolution of entrapped air bubbles. All samples fall, within error, on or above the projected region of ratios for dissolved excess air. Any samples above this region likely experienced partial air bubble dissolution during recharge. The one outlier below this region, well 7R3, does not fit a possible denitrification trend and this result can probably be explained as gas loss during sampling.

Figure 4. Stable isotopes of water. Three potential water sources include South Bay Aqueduct (SBA), modern precipitation, and local groundwater. Trendline represents linear regression of all groundwater data from this study. The inset demonstrates how Livermore well sample data compare to the Global Meteoric Water Line (GMWL) and to precipitation data collected at Santa Maria, CA, the nearest long term monitoring station (GNIP, 2004).

SBA: $\delta^{18}\text{O} = -10.6\text{‰}$ to -9.9‰ ; $\delta^2\text{H} = -79\text{‰}$ to -70‰ (Rees, 1994)

LLNL Precipitation: $\delta^{18}\text{O} = -7.9 \pm 2.8\text{‰}$; $\delta^2\text{H}$, unknown (pers. comm., T. Rose)

Groundwater: $\delta^{18}\text{O} = -7.4\text{‰}$ to -6.9‰ ; $\delta^2\text{H} = -53\text{‰}$ to -49‰ (Rees, 1994)

GMWL: $\delta^2\text{H} = 8.17 (\pm 0.07) \delta^{18}\text{O} + 11.27 (\pm 0.65) \text{‰}$ (VSMOW) (Rozanski, 1993)

Figure 5. Chloride vs. sulfate compositions. Three spatially distinct water types have been distinguished. Regions represented by well symbols are defined in Figure 2.

Figure 6. Nitrate concentrations and $\delta^{15}\text{N}$ values in groundwater. Expected $\delta^{15}\text{N}$ ranges for various sources are identified. Several samples from the wastewater region had $\delta^{15}\text{N}$ values off the scale of the chart, as indicated. Regions represented by well symbols are defined in Figure 2.

Figure 7. Nitrate concentration time series data. Drinking water maximum contaminant level (MCL) shown for reference. Well depths indicated. **(a)** Boundary Flowpath. **(b)** Alluvial Channel Flowpath.

Table 1. Well data and chemical and isotopic analyses of samples.

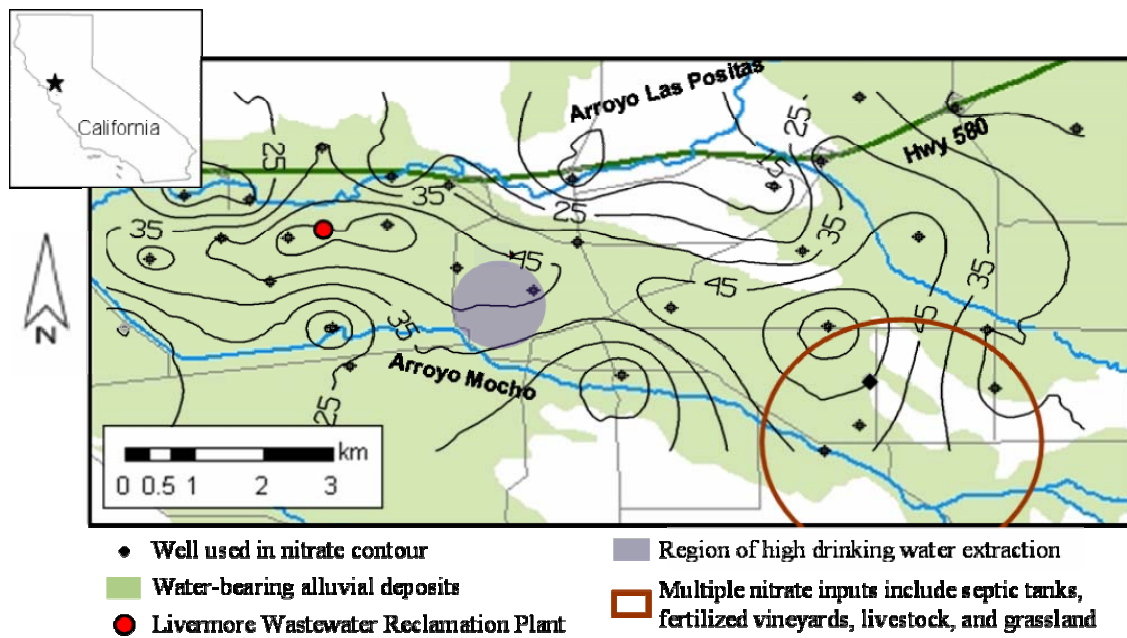


Figure 1. Nitrate concentrations in Livermore Valley.

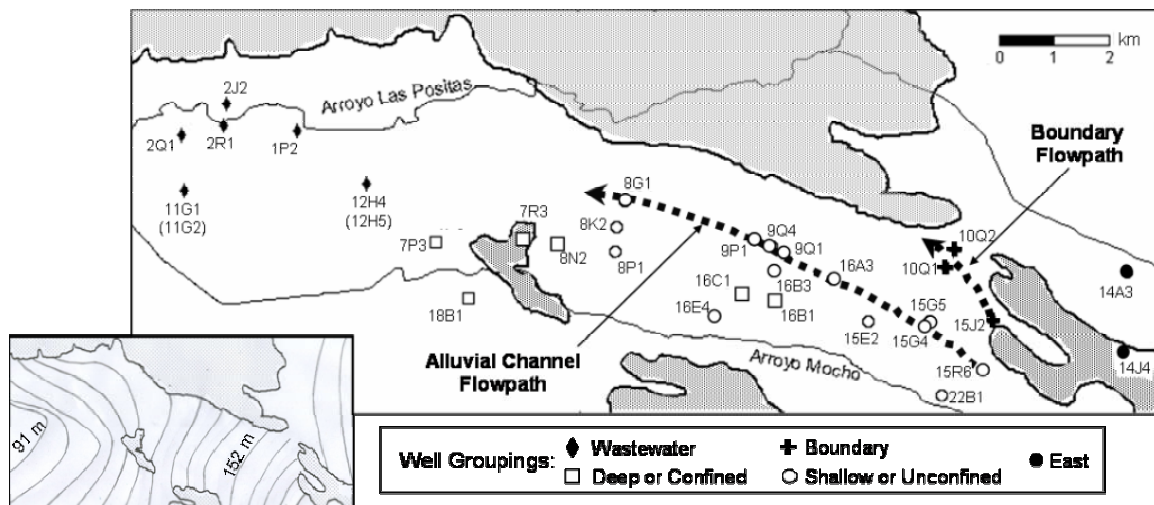


Figure 2. 2003 sampling locations.

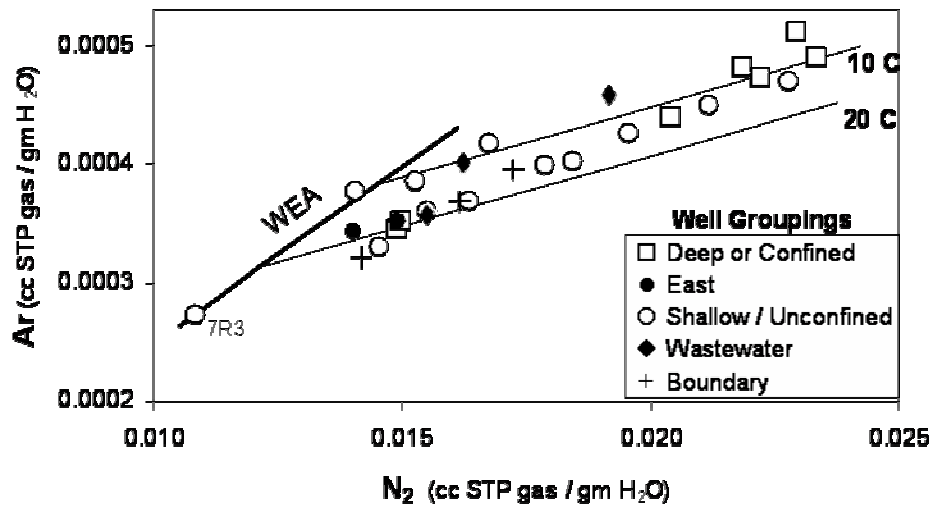


Figure 3. Dissolved nitrogen versus dissolved argon.

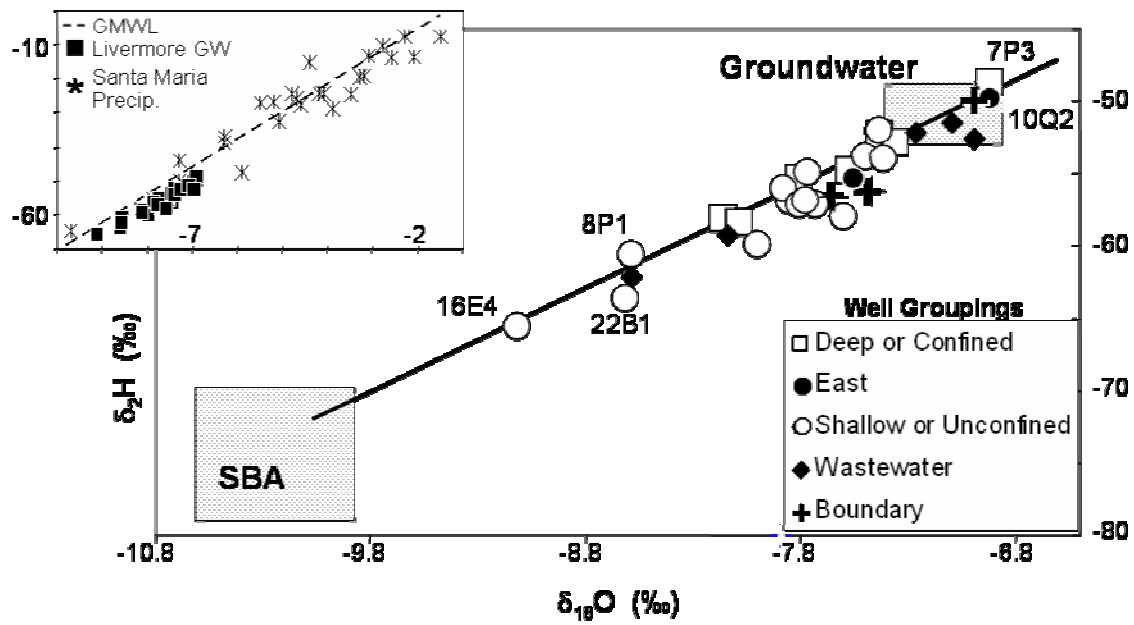


Figure 4. Stable isotopes of water.

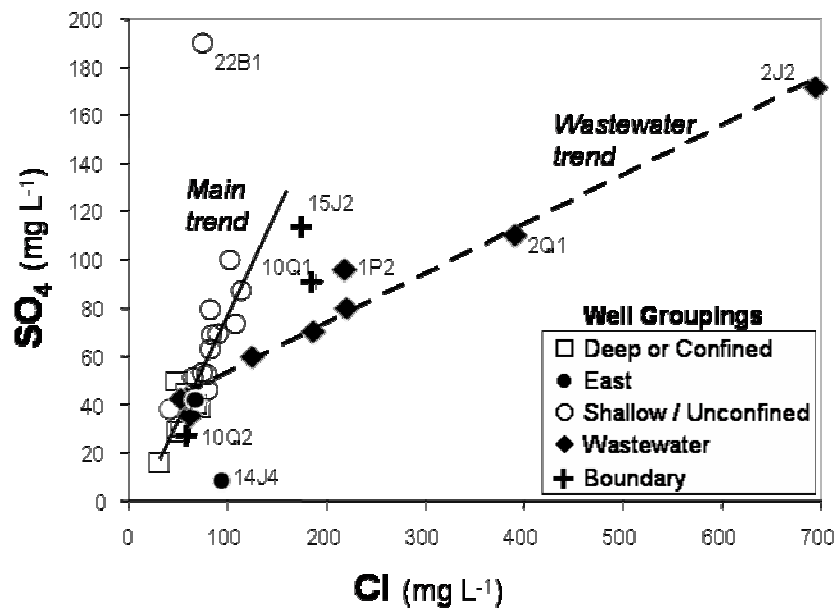


Figure 5. Chloride vs. sulfate compositions.

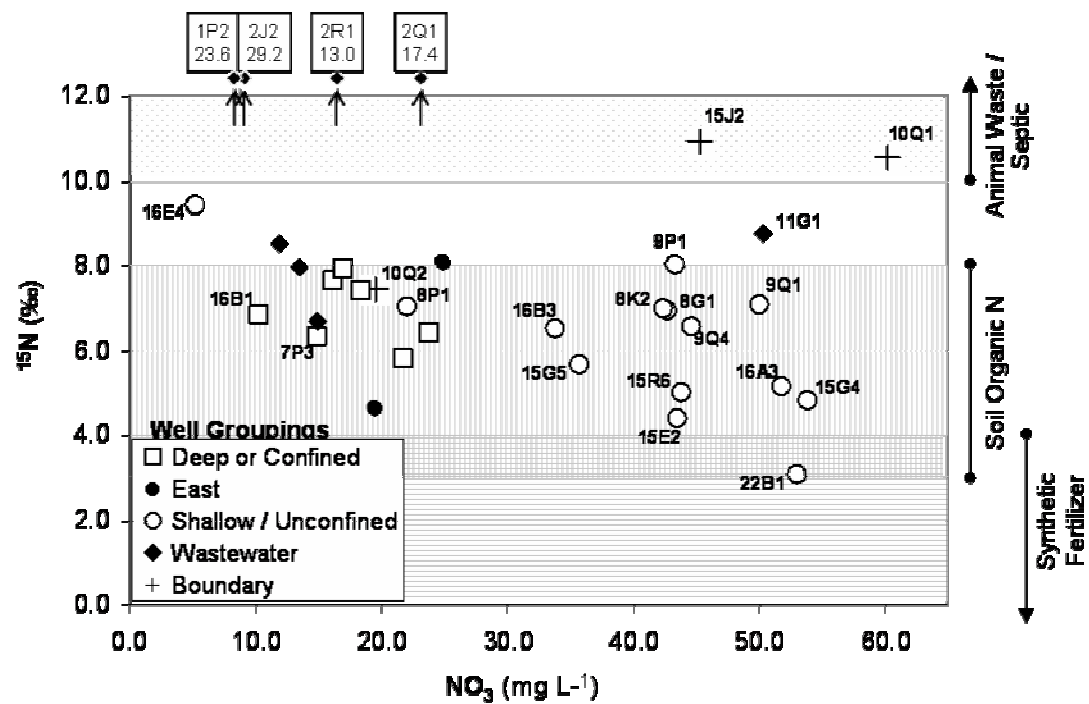


Figure 6. Nitrate concentrations and $\delta^{15}\text{N}$ values in groundwater.

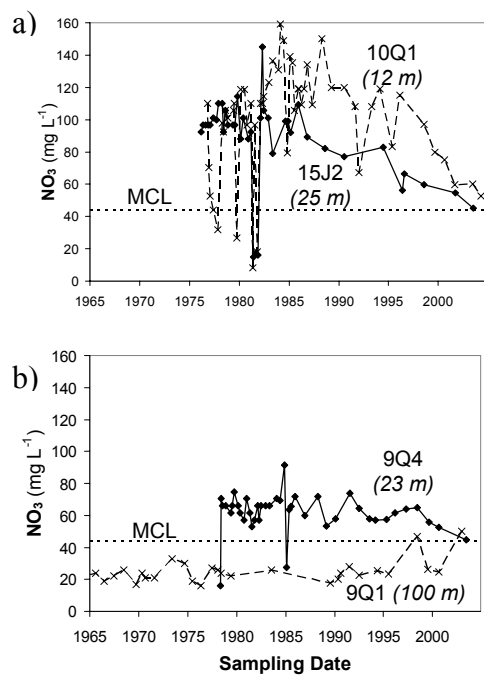


Figure 7. Nitrate concentration time series data.

Well ID	Well Type ^a	Well Screen ^b <i>m below surface</i>		NO ₃ ^c <i>mg/L</i>	$\delta^2\text{H}^c$ (H ₂ O) ----- <i>per mil</i> -----	$\delta^{18}\text{O}^c$ (H ₂ O)	³ H- ³ He age ^c <i>yr</i>	Recharge Temp <i>°C</i>	$\delta^{15}\text{N}^c$ (NO ₃) ---- <i>per mil</i> ----	$\delta^{18}\text{O}^c$ (NO ₃)	TOC ^c <i>mg/L</i>	Field DO ^c <i>mg/L</i>
1P2	MW	12.2	13.7	8.4	-53	-7.0	8	14.4	23.6	15.9	-	0.3
1P2	MW	same as above		8.2	-52 ^d	-6.9	-	-	23.6	14.7	-	0.6
2J2	MW	9.5	12.5	8.8	-51	-7.1	-	-	29.2	11.6	-	0.4
2Q1	MW	10.7	13.7	23.3	-52	-7.3	-	-	17.4	11.8	-	0.3
2R1	MW	6.4	7.9	16.6	-53 ^d	-7.3	-	-	13.0	6.7	-	0.9
7P3	PS	131.1	149.3^e	15.0	-49	-6.9	>50	11.8	6.3	4.0	0.36	-
7R3	PS	125.0	161.0	16.3	-53	-7.4	>50	15.1	7.6	6.8	0.51	-
8G1	PS	36.6	138.7	42.8	-55	-7.8	21	15.7	6.9	5.2	0.45	-
8K2	MW	19.5	21.0	42.5	-56	-7.9	10	19.8	7.0	3.6	-	-
8N2	PS	42.7	157.0	17.0	-58	-8.1	14	15.8	7.9	8.1	0.52	-
8P1	PS	37.2	80.2	22.1	-61	-8.6	9	15.5	7.0	4.8	0.57	-
9P1	PS	58.5	150.0	43.3	-52	-7.4	21	15.8	8.0	6.5	0.37	-
9Q1 ^f	PS	85.4	100.6 ^e	50.1	-54	-7.5	16	15.5	7.8	11.8	-	-
9Q4	MW	21.3	22.9	44.7	-57	-7.8	10	17.2	65	4.4	0.71	-
10Q1	MW	10.4	11.9	60.2	-56	-7.5	9	-	10.5	6.6	1.30	3.2
10Q2	MW	90.9	99.1	19.6	-50	-7.0	>50	-	7.4	6.6	0.20	-
11G1	MW	30.5	33.5	50.4	-53 ^d	-6.7	-	-	8.7	3.8	-	-
11G2	MW	70.1	103.7	12.0	-66 ^d	-8.8	-	-	8.5	6.0	-	-
12H4	MW	56.4	79.3	13.6	-62	-8.6	7	13.1	7.9	6.0	-	-
12H5	MW	109.8	118.9	15.0	-59	-8.1	12	-	6.7	8.3	-	-
14A3	MW	30.5	32.0	25.0	-55	-7.6	5	16.9	8.1	4.7	-	-
14J4	PV	30.5	71.6	19.5	-50	-6.9	<1	18.5	4.5	2.8	0.22	-
15E2	PV	31.7	57.6	43.5	-57	-7.7	16	19.7	4.4	2.8	0.50	-
15G4 ^f	PV	unk.; < 33.5		53.8	-60	-8.0	-	-	4.8	8.2	-	7.2
15G5 ^f	PV	12.2	30.5	35.7	-54	-7.4	-	-	5.7	10.9	-	-
15J2	PV	33.8	40.8^e	45.3	-57	-7.6	4	17.6	10.9	5.5	0.85	-
15R6	MW	unk.; < 17.7		43.8	-58	-7.6	-	-	5.0	3.1	1.05	4.4
16A3	MW	44.2	73.2 ^e	51.8	-57	-7.8	16	21.6	5.2	2.9	-	7.3
16B1 ^f	PS	42.7	118.9	10.3	-55	-7.8	18	-	6.8	12.1	-	-
16B1	PS	same as above		21.8	-58	-8.2	-	13.0	5.8	15.5	0.32	-
16B3	PV	0.0	24.4	33.8	-57	-7.9	-	20.4	6.5	3.0	0.74	-
16C1	PS	87.8	159.5	18.4	-55	-7.6	-	13.3	7.4	6.1	0.26	-
16E4	MW	10.7	12.2	5.2	-66	-9.1	<1	11.8	9.4	6.3	0.26	1.5
18B1	PS	57.9	141.8	23.9	-52	-7.4	11	14.5	6.3	6.0	0.30	-
22B1 ^f	MW	13.7	15.2	53.1	-64	-8.6	<1	-	3.1	8.1	-	7.6

^a MW = monitoring well; PS = public supply well; PV = private well.

^b Well depths indicated in **bold** are screened primarily in the Livermore Formation. All other wells are screened primarily in the alluvial layer.

^c Average Errors: NO₃ (±2.7%), $\delta^2\text{H}_{\text{H}_2\text{O}}$ (±0.9‰), $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (±0.1‰), ³H-³He age (±2 yr), $\delta^{15}\text{N}_{\text{NO}_3}$ (±0.3‰), $\delta^{18}\text{O}_{\text{NO}_3}$ (±0.9‰), TOC (±0.3 mg/L), field DO (±0.3 mg/L).

^d Measured at LLNL.

^e Longest of multiple screens. Also screened at: 7P3 – 91.5 to 97.6 m; 9Q1 – 3 8 m screens from 103.0 to 140.5 m; 15J2 – 23.2 to 24.7 m; 16A3 – 27.7 to 36.9 m.

^f Collected in 1/03. All other samples collected between 6/03 and 8/03. Multiple samplings at 1P2, in 6/03 and 8/03, and at 16B1, in 1/03 and 7/03.

Table 1. Well data and chemical and isotopic analyses of samples.

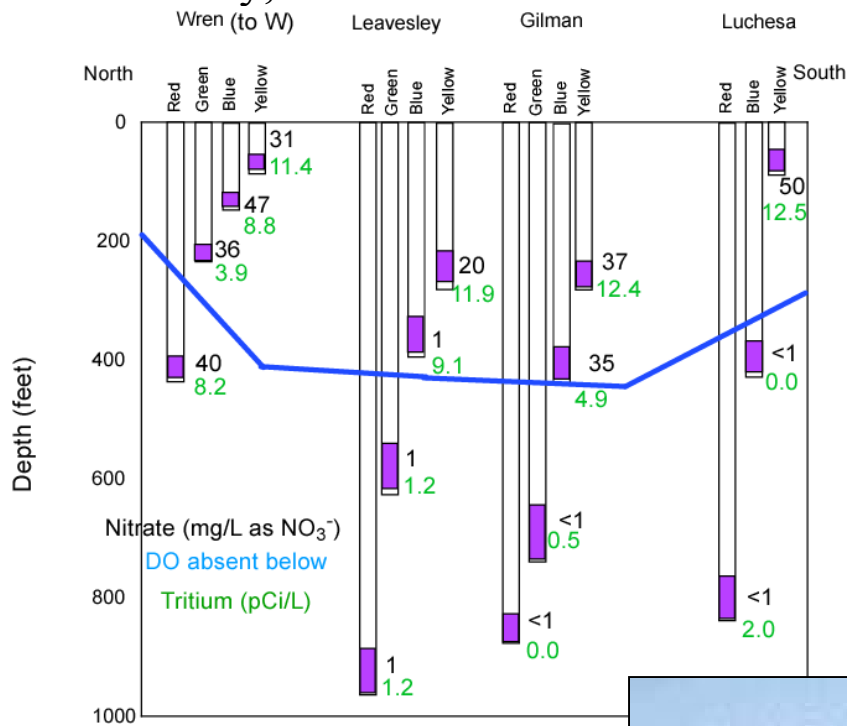
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LAWRENCE LIVERMORE NATIONAL LABORATORY



Prepared in cooperation with the
CALIFORNIA STATE WATER RESOURCES CONTROL BOARD

California GAMA Program: Sources and transport of nitrate in shallow groundwater in the Llagas Basin of Santa Clara County, California



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Sources and transport of nitrate in shallow groundwater in the Llagas Basin of Santa Clara County, California

Executive Summary

A critical component of the State Water Resource Control Board's Groundwater Ambient Monitoring and Assessment (GAMA) Program is to assess the major threats to groundwater resources that supply drinking water to Californians (Belitz et al., 2004). Nitrate is the most pervasive and intractable contaminant in California groundwater and is the focus of special studies under the GAMA program. This report presents results of a study of nitrate contamination in the aquifer beneath the cities of Morgan Hill and Gilroy, CA, in the Llagas Subbasin of Santa Clara County, where high nitrate levels affect several hundred private domestic wells.

The main objectives of the study are: 1) to identify the main source(s) of nitrate that issue a flux to the shallow regional aquifer 2) to determine whether denitrification plays a role in the fate of nitrate in the subbasin and 3) to assess the impact that a nitrate management plan implemented by the local water agency has had on the flux of nitrate to the regional aquifer. Analyses of 56 well water samples for major anions and cations, nitrogen and oxygen isotopes of nitrate, dissolved excess nitrogen, tritium and groundwater age, and trace organic compounds, show that synthetic fertilizer is the most likely source of nitrate in highly contaminated wells, and that denitrification is not a significant process in the fate of nitrate in the subbasin except in the area of recycled water application. In addition to identifying contaminant sources, these methods offer a deeper understanding of how the severity and extent of contamination are affected by hydrogeology and groundwater management practices. In the Llagas subbasin, the nitrate problem is amplified in the shallow aquifer because it is highly vulnerable with high vertical recharge rates and rapid lateral transport, but the deeper aquifers are relatively more protected by laterally extensive aquitards. Artificial recharge delivers low-nitrate water and provides a means of long-term remediation. Examination of nitrate concentration in relation to groundwater age indicates that the nitrate management plan has not yet resulted in a decrease in the flux of nitrate to the shallow aquifer in the areas tested.

Introduction and Background

Nitrate contamination of California drinking water supplies is pervasive— about 10% of California public drinking water supply wells produce water that exceeds the regulatory drinking water limit, and a much larger fraction produce water which approaches the limit (CA DHS, 2004). Nitrate contamination of groundwater is a growing concern for drinking water supplies not just in California, but also in many areas in the United States. Between 1993 and 2000, the U.S. Geological Survey's National Water-Quality Assessment program found that 9% of domestic supply wells and 2% of public supply wells exceeded the Environmental Protection Agency's maximum contaminant level (MCL) for drinking water of $45 \text{ mg NO}_3 \text{ L}^{-1}$ (10 mg L^{-1} as N) (Nolan et al., 2002). The human activities that contribute nitrate to groundwater – animal operations, crop fertilization, wastewater treatment discharge, septic systems – are ongoing and essential

to the industry and commerce of the State of California. Best management practices can mitigate source loading but not eliminate it. Furthermore, nitrate is expensive to remove from drinking water supplies, especially in public and private systems that rely on untreated groundwater and do not have the necessary water treatment infrastructure. These factors combine to make nitrate the greatest contaminant threat to California's drinking water supply.

The ultimate goal of the *Groundwater Quality Monitoring Act of 2001* (AB599) is the implementation of a comprehensive monitoring program to allow groundwater basin assessment. Assessment is a broad term, but encompasses assessing susceptibility of groundwater to contamination, characterizing current water quality in a basin, and predicting future water quality under different conditions. Because of the potential threat that nitrate poses to drinking water supplies, special studies are focused on basin-scale nitrate contamination. To meet these goals, basin assessment must consider the current inventory of nitrate in basin soils and waters, current and past source loading, groundwater recharge and transport, and nitrogen cycling in the soil, vadose and saturated zone. Nitrate occurs naturally, has relatively low-intensity point, distributed and nonpoint sources, and has a long history of introduction into the environment. Surface nitrogen loading has dramatically increased in the last 50 years, making groundwater ages a useful approach to assessing historical inputs and to determining the effectiveness of relatively recently implemented nitrate management plans.

This study focuses on the aquifers beneath the cities of Morgan Hill and Gilroy, CA, in the Llagas Subbasin of the Gilroy-Hollister Groundwater Basin, where high nitrate levels affect several hundred wells (figure 1). Deep, high capacity public drinking water wells have lower, but rising nitrate concentrations. This is a serious water supply problem because the region relies exclusively on groundwater for its drinking water, and at least 19 public supply wells are in the contaminated portion of this basin, although none has as yet had an MCL exceedence. In a study carried out by the local water agency, over 600 private domestic wells were tested for nitrate concentration, and more than 300 had MCL exceedences (SCVWD, 1998). A previous GAMA California Aquifer Susceptibility study in which public drinking water wells from Morgan Hill and Gilroy were tested for vulnerability parameters concluded that several wells in Gilroy are highly vulnerable to contamination based on observed young groundwater ages (Moran et al., 2004). The same study showed that wells screened exclusively in the deeper aquifers are much less vulnerable to contamination.

The main objectives of this study are: 1) to identify the main source(s) of nitrate that issue a flux to the shallow regional aquifer 2) to determine whether denitrification plays a role in the fate of nitrate in the subbasin and 3) to assess the impact that a nitrate management plan, implemented by the local water agency, has had on the flux of nitrate to the regional aquifer. Application of multiple analytical and isotopic techniques highlights the value of an integrated, multi-faceted approach. In addition, the degree of vertical transport of nitrate to deeper drinking water aquifers, as well as the potential for mobilizing accumulated nitrate during artificial recharge is evaluated. The latter two topics are relevant for evaluating two possible remediation strategies – pumping and

treating groundwater from shallow zones before it is transported to deeper zones, and increased artificial recharge of low-nitrate water.

Many studies have used ^{15}N and ^{18}O in nitrate as tracers for the source and fate of nitrate contamination (Choi et al., 2003). Because of the overlap of source isotope values and the variety of potential fractionation processes that affect nitrate, isotopes alone are not always sufficient to provide conclusive evidence of the contamination source (Choi et al., 2003 and Bohlke and Denver, 1995). A successful investigation of nitrate behavior and distribution must take into account the many environmental and historical factors that affect nitrate fate and transport. These include local hydrogeology, changing land use practices, and variable conditions that support an array of natural nitrogen cycling reactions (Kendall and Aravena, 2000). Combining the results of these techniques allows an understanding of nitrate contamination in a larger context and facilitates development of effective management strategies.

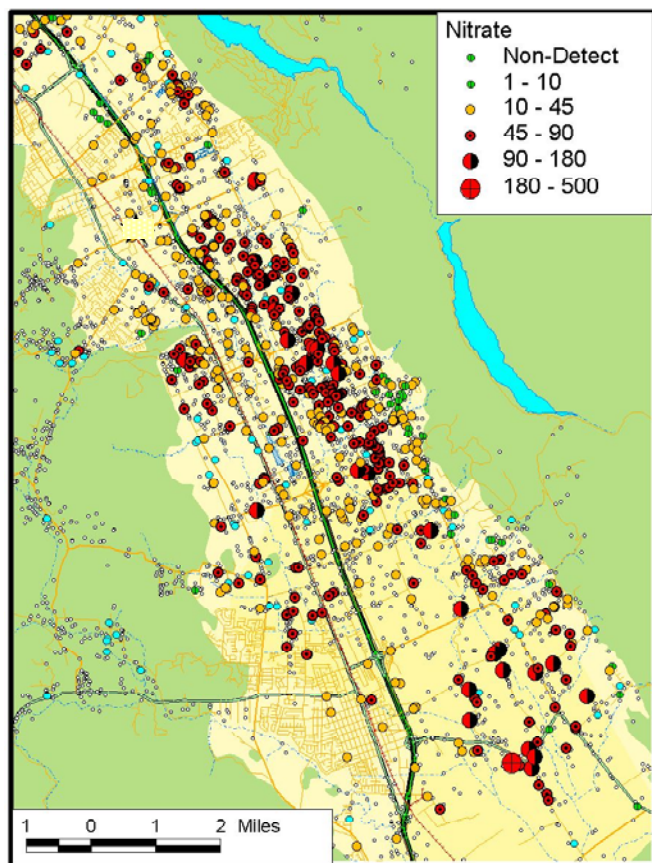


Figure 1 (courtesy of SCVWD). Maximum nitrate concentrations (mg/L as NO_3^-) observed in wells in the Llagas Basin.

This study demonstrates the application of an integrated analytical approach in a nitrate-impacted groundwater basin. Interpretation of nitrate ^{15}N and ^{18}O data to identify contamination sources is enhanced through the use of additional isotopic and chemical tracers. We use well water major ion analyses to delineate the scope of the high nitrate

region, and use historical data, collected for nitrate monitoring purposes, to track concentration changes through time. Stable isotopes of water provide information about groundwater sources, and residence time methods using tritium and noble gas measurements further constrain the source history. Possible reactions of nitrate are accounted for by analysis of dissolved gases, which can indicate whether saturated-zone denitrification has taken place. The methods used here could be widely applied in the many groundwater basins where urbanization has created a greater demand for drinking water, and where decades of agricultural activity have left a potential source of nitrate to groundwater.

Site Description and Land Use History

The groundwater basins of the Santa Clara Valley lie in an alluvial trough between the Santa Cruz Mountains on the west and the Diablo range to the east (figure 2a). The Santa Clara Valley Basin fills the southern end of the structural trough containing San Francisco Bay. South of the main subbasin, the Santa Clara Valley Basin narrows through Coyote Valley, then splays to the south with alluvial fan material from Coyote Creek to form the Llagas subbasin, part of the Gilroy-Hollister Valley Basin. Other major sources of alluvial fill material are from Llagas Creek and Uvas Creek off of the Santa Cruz Mountains to the west. Alluvial sediments are more than 1000 feet thick in the southern portion of the subbasin. The northern portion of the Llagas basin and the elevated lateral edges constitute the forebay, with unconfined conditions, recharge from subsurface inflow, percolation through streams, rainfall and irrigation returns, and flow toward the south-southeast, where the basin flattens out. Confining conditions begin at approximately Rucker Avenue (figure 2a), where upper and lower aquifer zones are separated by a major, laterally continuous aquitard that occurs at depths of 20 to 100 feet. The water-bearing materials in the subbasin consist of Pliocene to Holocene age unconsolidated to semi-consolidated alluvial deposits (CDWR, 1981). Discharge takes place at the Pajaro River to the south, and through pumping (CDWR, 1981).

The basin is managed for conjunctive use by the Santa Clara Valley Water District (SCVWD). Approximately 55,000 acre-ft is drawn for public water supply and irrigation from the Llagas and Coyote subbasins (SCVWD Groundwater Management Plan, 2002), with the majority coming from the Llagas subbasin. Artificial recharge includes controlled in-stream recharge during the dry season, and off-stream recharge in ponds that are either continuously recharged, or in ponds that are periodically dried. Beginning in 1983, water delivered to the recharge ponds has come from the San Luis Reservoir, which receives water from the Sacramento-San Joaquin Delta. Artificial recharge is therefore a combination of water imported from outside the study area, and locally-captured water. Natural recharge from rainfall (average annual rainfall in San Jose is 14.5 inches) and runoff occurs throughout the basin, and sources of non-natural uncontrolled recharge include leakage from pipelines, seepage through the boundaries of the groundwater basin, and net irrigation return flows.

Land use in the study area is approximately 40% agricultural, 25% urban, 20% rural residential, 5% open space and parks, and the remaining 10% of mixed use (1995 Santa Clara County General Plan). A gradual retiring of agricultural land to suburban housing

has taken place over the past 30 years. In rural residential areas, nearly every parcel has a septic tank for wastewater treatment, and a previous study (SCVWD, 1994) estimated potential nitrogen loading from septic tanks at 53 to 151 thousand pounds per year over the study area (Table 1). The other sources considered in the study were agricultural lands fertilized by commercial N-fertilizer (227,000 lb/yr), agricultural lands fertilized by cattle manure (8,000 to 30,000 lb/yr), rainwater (14,000 lb/yr), 4 existing dairies (4.6 to 6.9 thousand lb/yr), 20,000 to 50,000 cattle, including some small feed lots of up to 200 cattle (162,000 to 538,000 lb/yr assuming no waste management), 4 egg farms (one with 230,000 chickens; 90,000 to 151,000 lb/yr assuming no waste management), wastewater from three food packaging operations (3.5 to 5.2 thousand lb/yr), process wastewater from 2 wineries, wastewater from a cogeneration facility that converts agricultural waste into electrical energy, a sewage treatment facility (2.1 to 3.1 thousand lb/yr), and 602 acres of greenhouse operations (11,000 to 54,000 lb/yr). Several of the potential sources have decreased in number or extent in the study area over the past few decades. For example, before about 1970 several large feedlots with more than 2000 cattle existed in the area, and the number of dairies has likewise decreased from more than 20 to 4 since the 1960's. The study concludes that the two main sources are likely septic discharges and inorganic fertilizer from agricultural lands. Nursery crops, the highest cash crop produced in the area, and greenhouse operations are considered potentially large and growing contributors.

Table 1. Estimated potential nitrogen loadings to groundwater (SCVWD, 1996)

Source	Total Potential N Loading (thousands of pounds per yr)
Septic Tanks	53-151
Agricultural Lands Fertilized by Commercial N fertilizer	227
Agricultural Lands Fertilized by Manure	8.1-26.9
Rainwater	14
Dairies	4.6-6.9
Cattle Feed Lots	162-538*
Egg Farms	90-151
Food Packaging Operations	3.5-5.2
Cogeneration Facility	2.2-3.3
Sewage Treatment Facilities and disposal pits	2.1-3.8
Greenhouse Operations	11-54

* assuming no nitrate waste management

In 1997, SCVWD began implementation of a Nitrate Management Program based on a study of nitrate contamination in shallow groundwater that included an assessment of potential sources of nitrate (SCVWD, 1996). One of the main elements of the program consists of assisting growers in evaluating and adopting the use of in-field nitrate testing and N management planning to improve fertilizer use efficiency and profitability. Routine field monitoring and comparative trials utilizing in-field soil and petiole testing is carried out to confirm the utility of in-field soil nitrate testing for N-fertilizer

scheduling on crops with sprinkler or drip irrigation. Also, an evaluation of whether in-field quick soil and petiole testing could allow reduced fertilizer application for crops on drip systems for warm season crops like peppers was carried out at individual fields. In addition, educational resources and on-site soil and water testing are made available through use of a mobile lab, test kits are distributed to growers, and educational seminars are carried out at local schools and agricultural extension venues. The efficacy of the program in reducing nitrate flux to groundwater has not been assessed. Many of the activities associated with the program began in earnest in 2000, only four years before the time of sampling for this study.

METHODS

Sample Collection

The fifty-six well sampling locations are shown in Figure 2b and described in Table 2a. At SCVWD and South County Regional Wastewater Authority (SCRWA) monitoring wells, samples were taken using a portable submersible pump. At private domestic wells and City of Gilroy monitoring wells, dedicated well pumps were used. Most ion and isotope samples were filtered in the field with a 0.45µm in-line filter. Nitrate isotope samples were loaded onto anion exchange columns within 24 hours of sampling at LLNL, and ion analyses were performed within 48 hours of sampling. For excess nitrogen analyses, dissolved gases (nitrogen, oxygen, and argon) were collected in 40-mL vials (VWR TraceClean™, amber borosilicate; 0.125-inch septum liner) with no headspace. Samples were stored in coolers on ice and analyzed within 24 hours of sampling. A 1-L Pyrex bottle with a polypropylene plug seal cap was filled for tritium analysis and a 30-mL clear, French-square type glass bottle with a Qorpak™ polyseal-lined cap was filled for analysis of stable isotopes O and H in water. Approximately 10 mL of groundwater was collected in copper tubes pinched by metal clamps for noble gas samples.

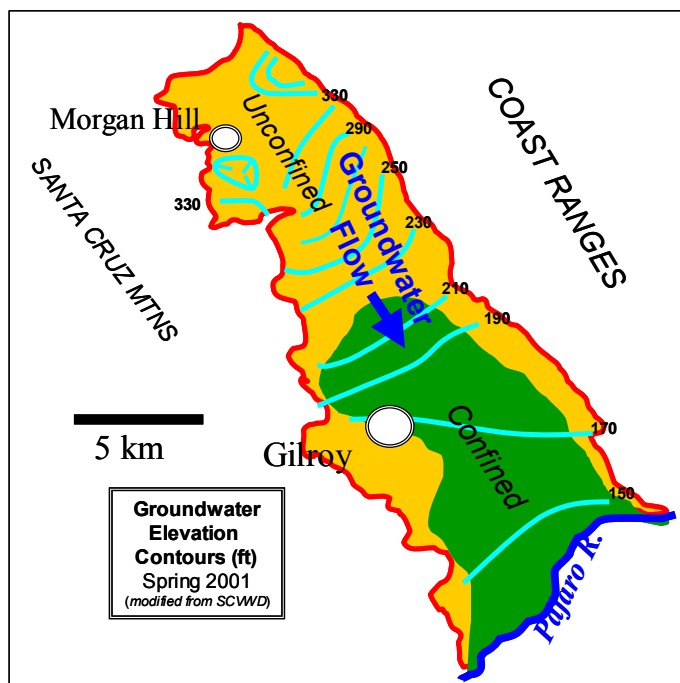


Figure 2a. Map of the Llagas subbasin showing subbasin boundaries, major geographic features and groundwater elevation contours for Spring, 2001 (after SCVWD).

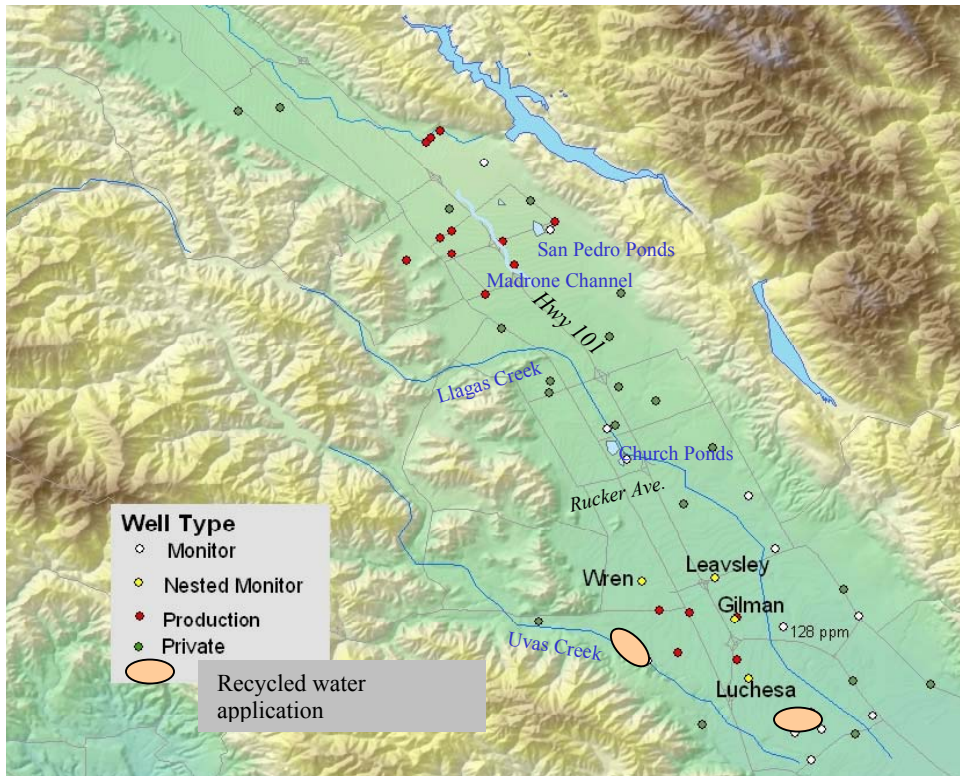


Figure 2b. Map showing wells sampled for the study. Named wells and recharge areas are referred to in the text.

Laboratory Methods

Nitrate isotope samples were analyzed at the Environmental Isotopes Lab at the University of Waterloo, all other analyses were performed at LLNL. After extraction as silver nitrate, nitrogen gas for the measurement of $\delta^{15}\text{N}$ was produced by the sealed tube Cu/copper oxide method (Kendall and Grim, 1990; Flatt and Heemskerk, 1997) and CO_2 for measurement of $\delta^{18}\text{O}$ was produced by combustion with graphite. The isotope ratios of these gases were measured on a PRISM isotope ratio mass spectrometer. $\delta^{15}\text{N}$ results are reported as per mil relative to AIR and $\delta^{18}\text{O}$ results are referenced to VSMOW. Anions and cations were measured by ion chromatography on a Dionex IC DX-600 with a precision of $\pm 2.7\%$ relative standard deviation for nitrate. Oxygen isotopes of water were measured on a VG PRISM isotope ratio mass spectrometer. Results are reported as per mil with reference to VSMOW and have a precision of $\pm 0.1\text{‰}$. Deuterium was measured on the VG PRISM after extraction of hydrogen by the zinc reduction technique. Results are reported as per mil with reference to VSMOW and have a precision of $\pm 0.9\text{‰}$. Dissolved gases for examination of excess nitrogen were measured by membrane inlet mass spectrometry (MIMS) with an SRS RGA200 quadrupole mass spectrometer (Kana et al., 1994). ^3He and ^4He were measured on a VG5400 mass spectrometer, Ar was measured using a high-sensitivity capacitive manometer, and Ne, Kr, and Xe were measured on an SRS RGA200 quadrupole mass spectrometer. Tritium was determined by measuring the rate of ^3He accumulation. Residence time calculations were made by combining measurements of tritium with measurements of its decay product, ^3He , and excess air was determined from measured Ne concentrations. In this

calculation, noble gas data was used to separate tritiogenic helium from that from other sources (Ekwurzel, 2004).

Isotope and Dissolved Gas Techniques

A variety of nitrate fractionation processes lead to unique isotopic signatures for different nitrate sources. As a result, isotope values of nitrogen and oxygen can be useful in identifying the origin of groundwater nitrate (figure 3). Synthetic fertilizers generally have $\delta^{15}\text{N}$ values between -2‰ and $+4\text{‰}$ (Kendall et al., 1998). By the time it reaches the groundwater, however, fertilizer nitrogen tends to be enriched by several per mil over the original source, often making it indistinguishable from soil organic nitrogen, which tends to have $\delta^{15}\text{N}$ values of $+3\text{‰}$ to $+8\text{‰}$ (Bohlke and Denver, 1995). Due to volatile loss of ammonia from manure, nitrate from animal waste has higher $\delta^{15}\text{N}$ values, usually greater than $+10\text{‰}$, and so can often be distinguished from other sources. All animals produce waste with similar $\delta^{15}\text{N}$ values, though, so isotopes alone are usually not useful in differentiating between septic waste and other animal wastes (Kendall, 1998; Choi et al., 2003).

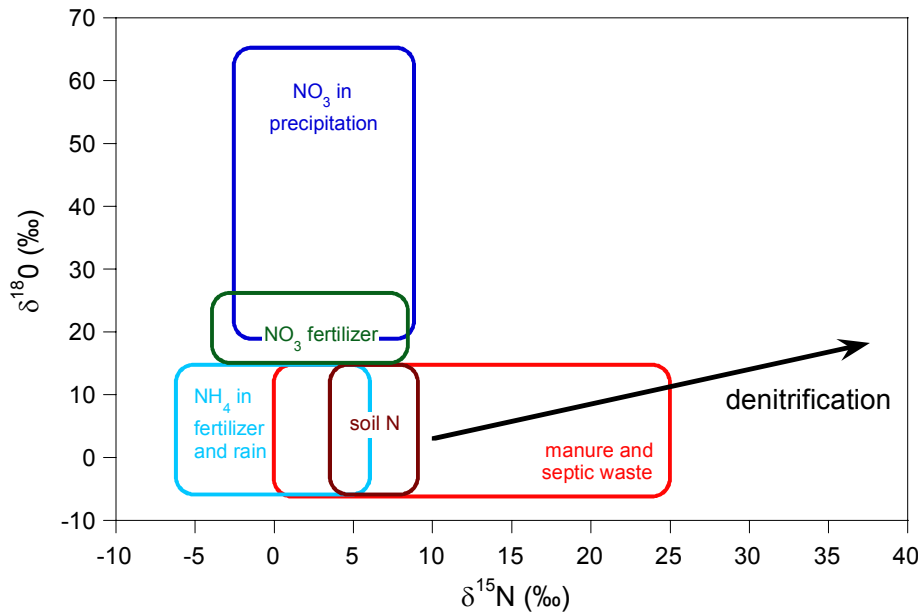


Figure 3: Isotopic composition of nitrogen and oxygen in nitrate from different sources (after Kendall, 1998).

Oxygen isotope values of nitrate can help clarify source identification, especially to separate nitrate fertilizer input from other sources, which produce nitrate by nitrification of ammonium or organic nitrogen. The $\delta^{18}\text{O}$ in nitrate fertilizers has a value close to the atmospheric value of $+23\text{‰}$. Other sources of nitrate incorporate two oxygen atoms from water and one from dissolved oxygen gas, leading to lighter $\delta^{18}\text{O}$ values dependent on the

oxygen isotopes in the water (Kendall and Aravena, 2000). Nitrate from ammonium nitrate fertilizers will have $\delta^{18}\text{O}$ values that reflect both processes (Aravena et al., 1993).

Nitrate isotope data are also valuable as indicators of the occurrence of denitrification; as denitrification occurs, nitrogen and oxygen in nitrate are enriched in a characteristic 2:1 ratio (Kendall, 1998). Saturated zone denitrification can also be identified by the presence of its end product, excess nitrogen, dissolved in groundwater. Atmospheric nitrogen is distinguished from excess nitrogen by comparison with dissolved argon, the dominant source of which is atmospheric (Kana et al., 1994; Vogel et al., 1981). We employ both methods to check for possible denitrification.

Geochemical Modeling

Geochemical modeling, using the U.S. Geological Survey's PHREEQC geochemical model (Parkhurst and Appelo, 2002), was used to identify and explain trends in the water quality parameters (major cations, anions, and pH) that correlated with nitrate concentrations and other sample attributes to assist in identifying source signatures. PHREEQC's inverse geochemical modeling capability was utilized to understand the role of carbonate mineral equilibration (calcite, dolomite) in buffering water chemistry in response to possible acidification reactions involving oxidation of NH_3 and/or associated organic material as part of a putative nitrate source loading model.

RESULTS AND DISCUSSION

Nitrate occurs at high concentrations in shallow-screened wells

Historically, nitrate contamination is greatest in wells east of Highway 101, in the central and southern portions of the subbasin, where a large fraction of the wells have had concentrations above the MCL (figure 1). In data collected for this study (Table 2a,b,c), concentrations higher than expected for pre-development levels occur across the subbasin but the highest concentrations are recorded in the southeastern portion of the study area. The origin of the contamination is not clear from concentration patterns, and some of the highest concentrations recorded during the study are in the confined portion of the basin, not in the recharge areas to the north. Current and historical data consistently record higher nitrate concentrations in shallow monitoring and domestic wells than in deep wells. This is illustrated in figure 4, in which wells with top perforations above 250 ft may have high or low nitrate concentrations, but wells with top perforations deeper than about 250 ft have near-zero nitrate concentrations (with one exception at the deep Wren well).

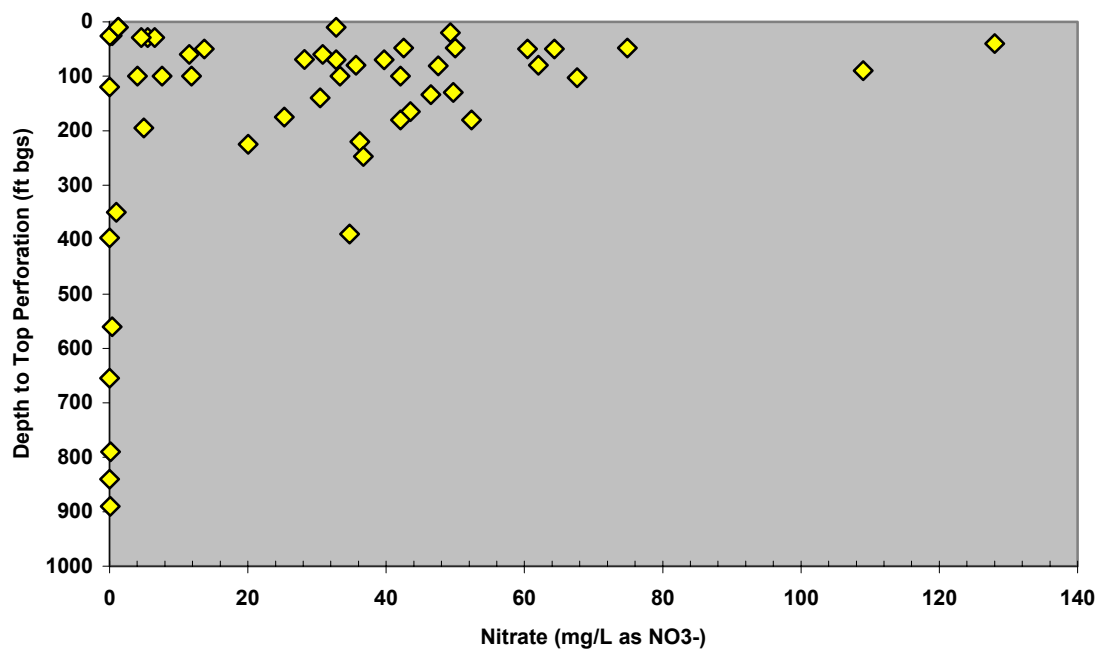


Figure 4. Nitrate concentrations measured in wells from figure 2b versus depth to top perforation show that anthropogenic nitrate does not occur in the deep aquifer.

Several geochemical parameters (dissolved oxygen, tritium, and some major ions) in addition to nitrate exhibit vertical stratification, which is most clearly observed in the nested monitoring wells in Gilroy (figure 5). The four sets of nested monitoring wells owned by the City of Gilroy are particularly useful - they allow examination of parameters' spatial patterns in 3 dimensions and are located in contaminated areas. Chemically stratified groundwater could be the result of a transition to reducing conditions at depth, in which case denitrification could potentially account for the observed drop in nitrate concentrations. As illustrated in figure 5, dissolved oxygen concentrations drop off sharply below about 400 ft in the center of the subbasin and below about 200 ft on the basin margins. Similarly, however, tritium concentrations abruptly decrease to less than 1 pCi/L at the same depths. (An exception occurs at the Wren site where young, nitrate-laden water is found at 400 ft.) The transition from high nitrate to low nitrate groundwater could therefore be due to hydrogeologic factors; i.e., the presence of laterally extensive aquitards with recently recharged, nitrate contaminated groundwater above, physically isolated from old, 'pristine' groundwater below. In the latter case, the time scale for recharge to the deep aquifer, and the heterogeneity of the aquifer system become important factors for predicting the fate and transport of nitrate on a basin scale.

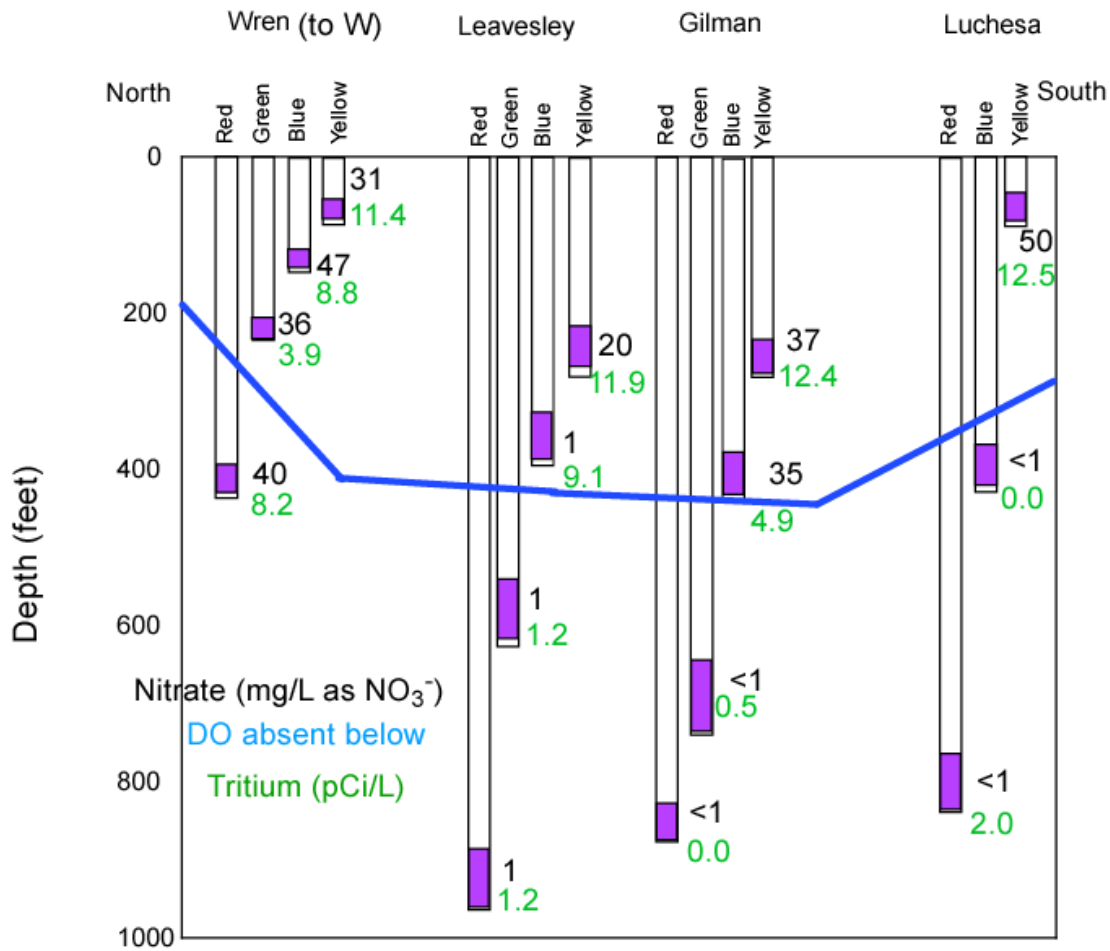


Figure 5. Schematic cross section showing screened intervals (in purple) of nested monitoring wells in Gilroy. Groundwater is stratified with respect to nitrate, tritium, and dissolved oxygen (blue line signifies depth below which dissolved oxygen is near-zero).

CO₂ partial pressure values (P_{CO2}) were estimated using PHREEQC from pH and major ion concentration measurements (the quantity of HCO₃⁻ in each water sample was not directly measured but was inferred by charge balance). Elevated P_{CO2} would be expected in association with vegetation occurring in recharge areas (as a result of microbial respiration in the root zone) or, in particular, from mineralization of organic carbon associated with manure and/or septic discharge. The distribution of calculated P_{CO2} values suggests a significant fall-off with depth (Figure 6), with the highest values generally occurring in the southeast portion of the subbasin where well screens are generally the shallowest. However, a clearly discernable trend between nitrate concentrations and P_{CO2} is absent (Figure 7). As such, the calculated P_{CO2} values probably do not support manure and/or septic discharge as being dominant sources of nitrate in the water samples studied.

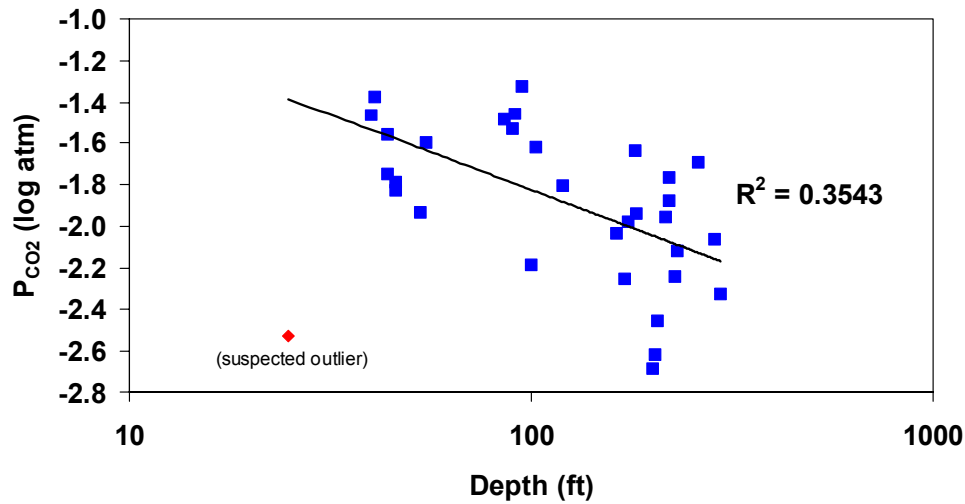


Figure 6. Calculated CO₂ partial pressures vs. well depth.

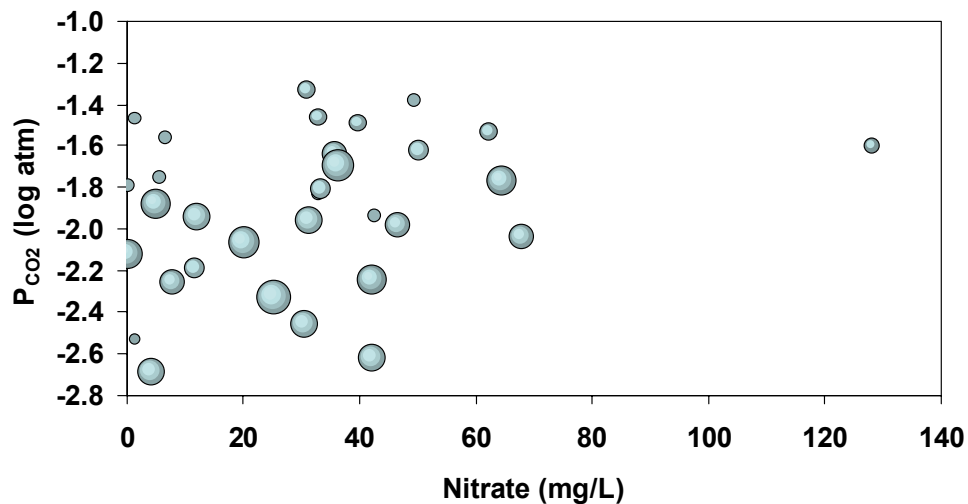


Figure 7. Observed nitrate concentrations, calculated CO₂ partial pressures, and well depth (width of circles corresponds to well depth).

Time series reconstructions of past nitrate concentrations at individual wells using SCVWD's monitoring data show statistically significant upward trends from the 1960's to the present in many of the wells from the affected areas (SCVWD, 1998). Superimposed on the long term upward trend is a seasonal cycle with wintertime highs and summertime lows in several affected wells (Figure 8). In general, the most recent data (collected in August, 2004) continue to show flat or slightly increasing trends, when compared with previous summertime results. This observation is noteworthy because a nitrate management plan has been in place since about 1997. The pattern displayed at individual wells suggests that a store of nitrate is present in the shallow vadose or soil zone, and is intercepted during the winter when water levels rise due to decreased local and regional pumping and increased precipitation. This could also explain the continuing

increase in concentrations with time even though loading may have decreased in response to the nitrate management plan. Alternatively, the observed seasonal pattern could result from late-season irrigation or leaching from fallow fields during the rainy season. Those processes flush accumulated excess nitrate from fertilizer through the soil zone to shallow groundwater.

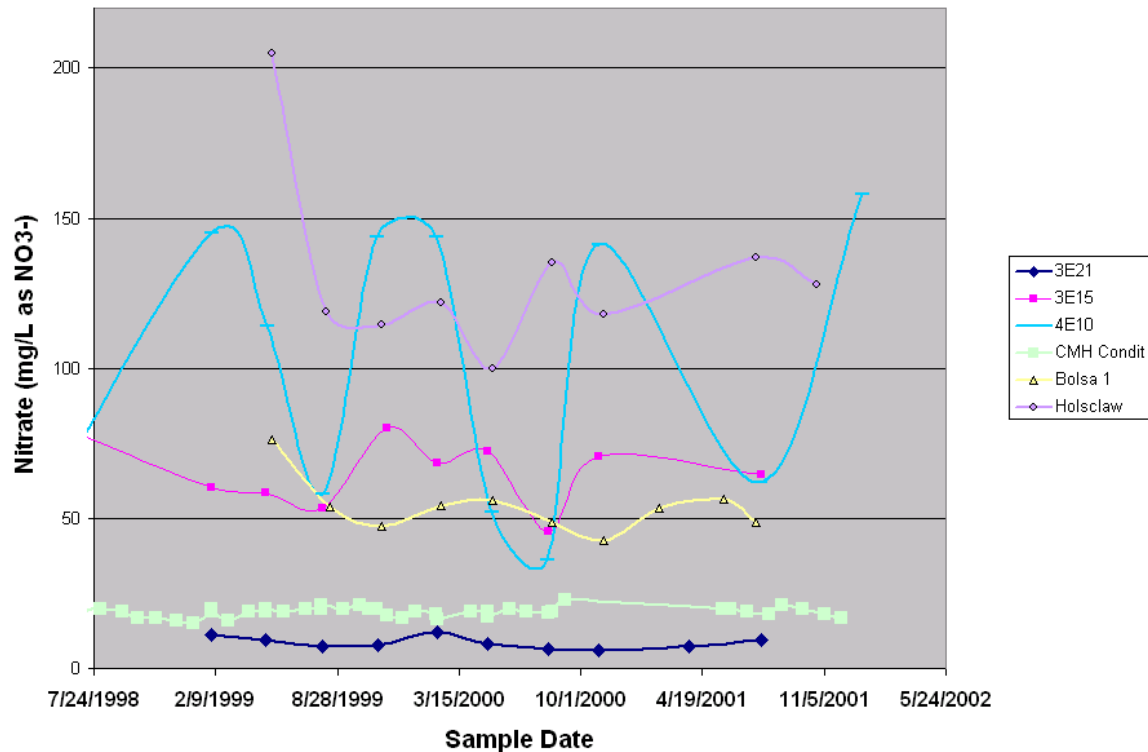


Figure 8. Measured nitrate concentrations show seasonal variations, especially in wells with shallow top perforations in the southern portion of the basin.

Isotopes of water and groundwater ages reveal distributed recharge of local and imported water

Stable isotopes of the water molecule help to establish groundwater provenance, while tritium-helium is used to determine groundwater residence time; both stable and radioactive isotopes of water can help delineate recharge areas, groundwater flowpaths, and nitrate sources. The $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ positions of all of the 2003 data fall below the Global Meteoric Water Line and have a trend generally parallel to it, providing little evidence of evaporation on a large scale. Exceptions are the two wells adjacent to artificial recharge ponds (Church 457, Church 452, see figure 2b) and one of the wells in the wastewater application area (Obata 22), which show evidence for significant evaporation. Two other wells adjacent to the San Pedro recharge ponds are depleted compared to most well values, indicating the presence of imported water. Recharge water in the subbasin is a combination of locally-derived precipitation and runoff from within the watershed and imported San Felipe Project (SFP) water, which is transported

from the Sacramento-San Joaquin Delta and artificially recharged in Madrone Channel and in off-stream recharge facilities. Locally derived water in this relatively warm, low-lying subbasin has an observed range in $\delta^{18}\text{O}$ of -5‰ to -7‰ (Coplan and Kendall, 2000). Originating mostly in the northern Sacramento River watershed at high elevations, the imported water is isotopically lighter than local precipitation (-10.6‰ to -9.9‰ $\delta^{18}\text{O}$; $n = 2$). Imported SFP water recharges the aquifer in the Madrone Channel, San Pedro ponds and Main Avenue ponds. Wells with $\delta^{18}\text{O}$ values of less than -7‰ likely produce a component of this imported water. As seen in figure 9, these wells occur near artificial recharge areas in the northern part of the study area, and in shallow wells near Llagas Creek. Local water is delivered to Church Avenue ponds.

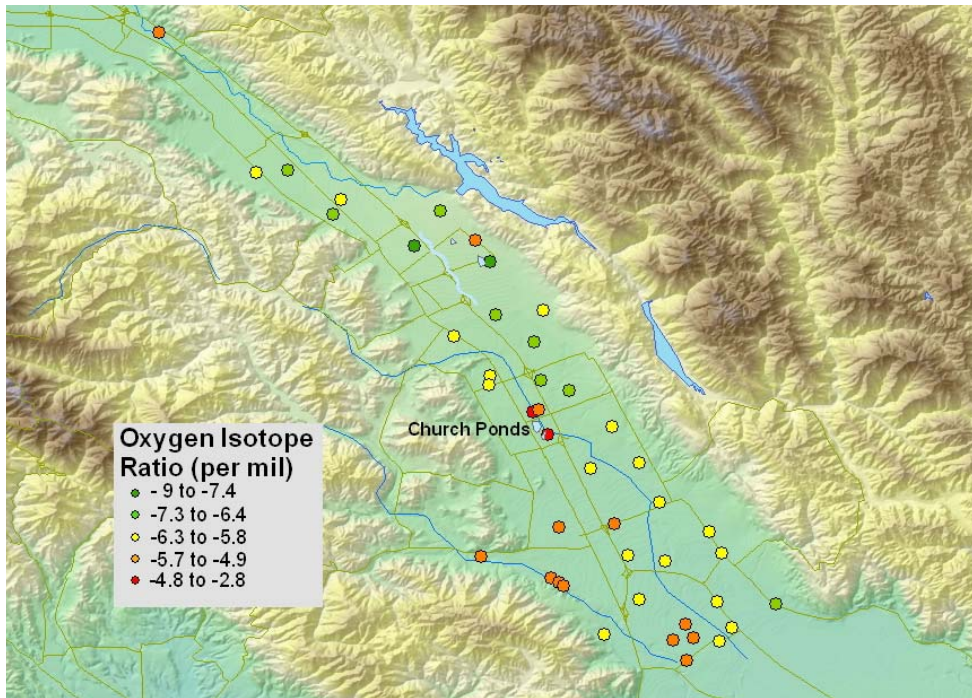


Figure 9. Observed oxygen isotope ratios show the influence of isotopically-enriched evaporated water recharge near Church Ponds and isotopically-depleted imported water in other wells where artificial recharge water comprises a component of groundwater.

A plot of $\delta^{18}\text{O}$ versus nitrate reveals that wells recharged by imported water (depleted $\delta^{18}\text{O}$ values), and wells recharged by evaporated water (enriched $\delta^{18}\text{O}$; from recharge ponds) have extremely low nitrate concentrations (figure 10). All of the wells with high nitrate concentrations have local water stable isotope signatures, indicating that nitrate source areas do not coincide with areas of artificial recharge. Imported Sacramento-San Joaquin Delta water itself contributes little nitrate, with an average concentration over the last 10 years of 2.5 mg L^{-1} (State of California, Department of Water Resources, Water Data Library, Water Quality Data).

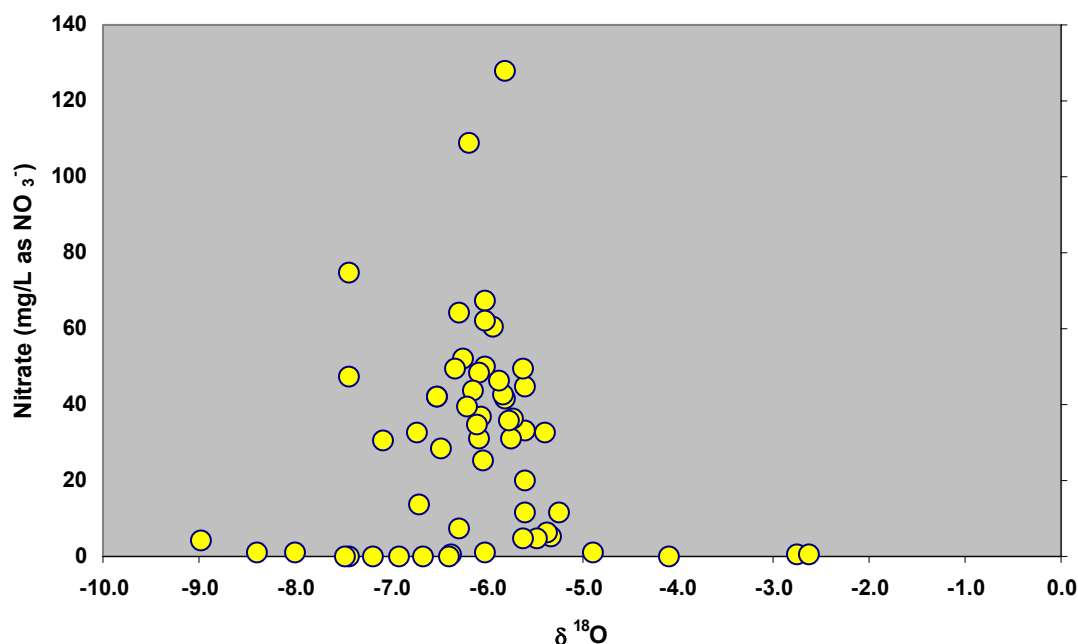


Figure 10. High nitrate concentrations in wells with ‘local’ isotopic ratios suggest that nitrate source areas do not coincide with artificial recharge areas.

Tritium concentrations and tritium-helium age data (Table 2c and figure 11) reveal a very dynamic shallow aquifer flow system, with significant recharge and relatively rapid groundwater flow over a large part of the subbasin. Tritium concentrations are remarkably uniform and in good agreement with the expected concentration in modern day precipitation. Thirty-five of fifty-five samples analyzed for tritium fall in the narrow range of 9 to 14 pCi/L (figure 12). Nineteen of these samples have $^3\text{He}/^4\text{He}$ ratios in the narrow range of 1.35×10^{-6} to 1.41×10^{-6} (close to the value expected for water in equilibrium with air and no tritiogenic ^3He), and corresponding calculated tritium-helium ages of less than 10 years. Wells along Uvas Creek (Christmas Hill, Thomas) and on the basin margins (Buena Vista, Leavesley 1), along with wells adjacent to artificial recharge facilities (Maple, San Pedro, Church, Coleman, Coyote Narrows, and Obata) have residence times of less than three years, and delineate the areas of active recharge.

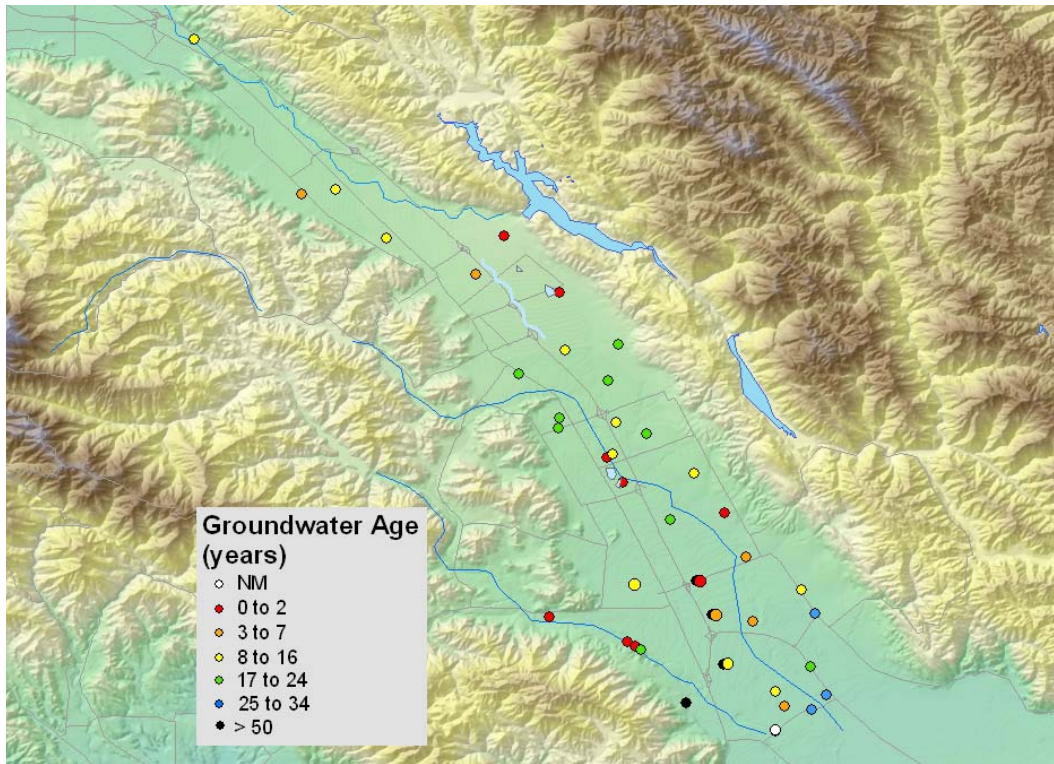


Figure 11. Very young calculated tritium-helium groundwater ages occur over a large portion of the basin and indicate high groundwater contamination vulnerability and active recharge to the shallow aquifer. For nested monitoring wells, the symbol on top is for the shallowest well – the deepest intervals have non-detectable tritium (> 50 year ages), but also have dissolved helium isotope ratios that reflect a mantle helium component.

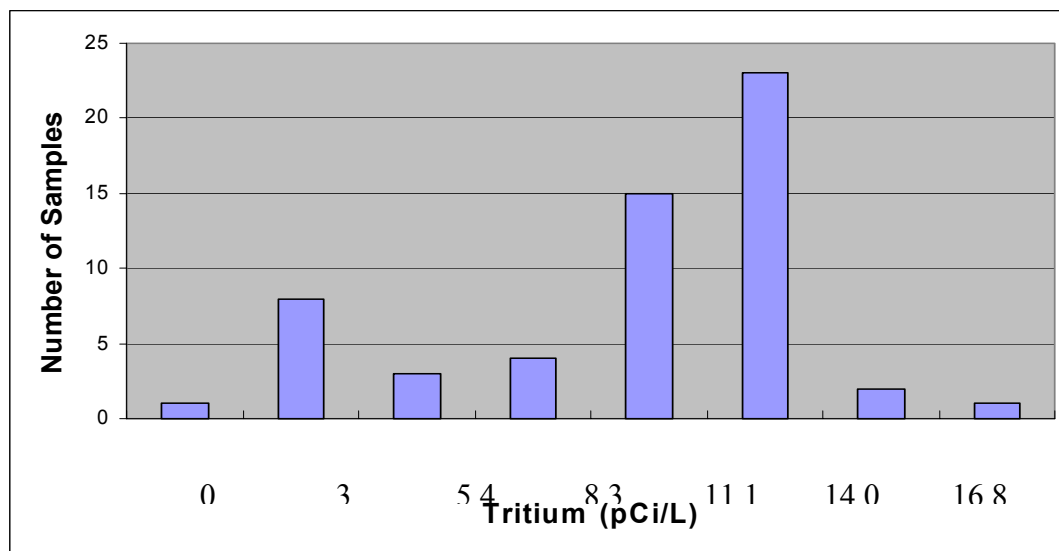


Figure 12. Histogram showing the prevalence of wells that produce groundwater with near modern tritium concentrations (8 to 14 pCi/L).

Significant, active recharge along Uvas Creek is further evidenced by very low excess air concentrations and low recharge temperatures observed in the wells adjacent to the creek. Low excess air is characteristic of stream recharge wherein the streambed meets the local water table and interaction between infiltrating water and vadose zone gas is minimal. Noble gas recharge temperatures for most wells in the study area cluster around 16C, the approximate mean annual air temperature, while wells along Uvas Creek have recharge temperatures of about 13C. The lower temperatures point to wintertime recharge when flows are high and streambeds are scoured of fine sediment that can inhibit recharge.

The shallowest wells in the three nested sets along the valley axis in Gilroy all have very young ages, indicating that the area of active recharge and rapid groundwater flow extends to the center of the subbasin. Most significantly, the wells with the highest nitrate concentrations, including Holsclaw, Leavesely 1, and Buena Vista 1, all have young groundwater ages (4 yr, 1yr, and <1 year, respectively), which means that a high nitrate flux to groundwater is ongoing in areas of 'natural recharge'. A major source of recharge in these areas may be irrigation return flow, so rapid recycling of high-nitrate groundwater used for irrigation is a plausible scenario.

Lateral flow in the shallow zone is therefore quite rapid, with significant spatial variability in the flow rate. An increasing groundwater age gradient that could be used to delineate lateral flowpaths is not evident, and recharge to the shallow system, while significant at artificial recharge areas, is widely dispersed. A sampling of flow velocities along possible flowpaths, determined from tritium-helium ages, exhibits a wide range. From the Buena Vista well to downgradient Leavesley 1, a flow velocity of approximately 1300 ft/yr is calculated, while a flowpath to the shallow Gilman well from Llagas Creek gives a velocity of approximately 6000 ft/yr. Vertical flow rates, determined from groundwater ages at the nested wells Maple 1 and 2 and Gilman are 5.3 ft/yr and 4.3 ft/yr, respectively.

Longer groundwater residence times indicate a less active flow regime and more distant recharge. In the Llagas subbasin, several wells in the northern area east and west of the main basin axis between Madrone Channel and Church Ponds recharge facilities have groundwater ages greater than 20 years (figure 11). Similarly, a group of 5 wells in the southeastern corner of the study area have distinctly older mean groundwater ages, and indicate that the area is likely fully confined with slower groundwater flow. Six wells (5 are deep, nested monitoring wells) in the study area have a component of dissolved gas from the earth's mantle, indicating upwelling of deep fluids with a primordial Helium isotope signature. As mentioned above, wells screened exclusively below 200 ft (including 4 of the 5 with a mantle He component) have no detectable tritium, indicating residence times of greater than 50 years. These wells provide an archive of groundwater that is not influenced by modern human activity. Wells with long screened intervals invariably produce groundwater with a broad age distribution – a mixture of tritiated nitrate-laden water combined with a component of tritium and nitrate-free water. For example Crumrine, a well with a nitrate concentration of 109 mg/L and $\delta^{15}\text{N}$ of 6.1‰ (suggesting a synthetic fertilizer source as described below), has a long well screen and a resulting mean age of 16 yr. This well draws in young groundwater, contaminated with

nitrate, along with a calculated 60% fraction of 'pre-modern' water, which likely adds little if any nitrate (Table 2c).

Nitrate in the most contaminated wells has a fertilizer source signature

Major dissolved gases were analyzed in order to test for the possible presence of excess dissolved nitrogen in groundwater. Dissolved nitrogen and argon trends do not show the presence of detectable excess nitrogen, demonstrating that saturated zone denitrification is not prevalent (Table 2b). This result is consistent with low dissolved organic carbon concentrations (< 1.5 mg/L TOC; $n=8$); a sufficient flux of organic carbon is necessary for heterotrophic denitrification. With the exception of the wells just adjacent to recharge ponds, shallow-screened wells in the study area have high dissolved oxygen concentrations that indicate an aerobic system with low reduction potential. Groundwater nitrate isotope data, therefore, may be interpreted directly as indicative of nitrate source, without accounting for enrichment due to denitrification along the flowpath.

Nitrate- $\delta^{15}\text{N}$ results, plotted in Figure 13, help identify the major sources of nitrate in wells from the study area. Wells in the southwestern portion stand out as having high nitrate- $\delta^{15}\text{N}$ and relatively low nitrate concentrations. Their higher nitrate- $\delta^{15}\text{N}$ values suggest an animal waste source. As noted above, application of recycled water from the SCRWA is applied to agricultural fields at Obata Farms, adjacent to the wastewater treatment facility, and at Christmas Hill Park in Gilroy. Three wells at each of those locations show evidence for a different source of nitrate than the rest of the study area. In addition, two other wells (Bolsa-2 and Bloomfield-1) in the southwest area near the areas of recycled water irrigation are likely affected by recycled water recharge, as evidenced by relatively high measured $\delta^{15}\text{N}$. The $\delta^{15}\text{N}$ values, though not as high as the range expected for treated wastewater effluent (between 13.0‰ and 29.2‰), are at least 2‰ higher than the narrow range observed outside of the area of recycled water application. The measured values may reflect a mixture of the recycled water source and a soil or fertilizer source that is less enriched in $\delta^{15}\text{N}$.

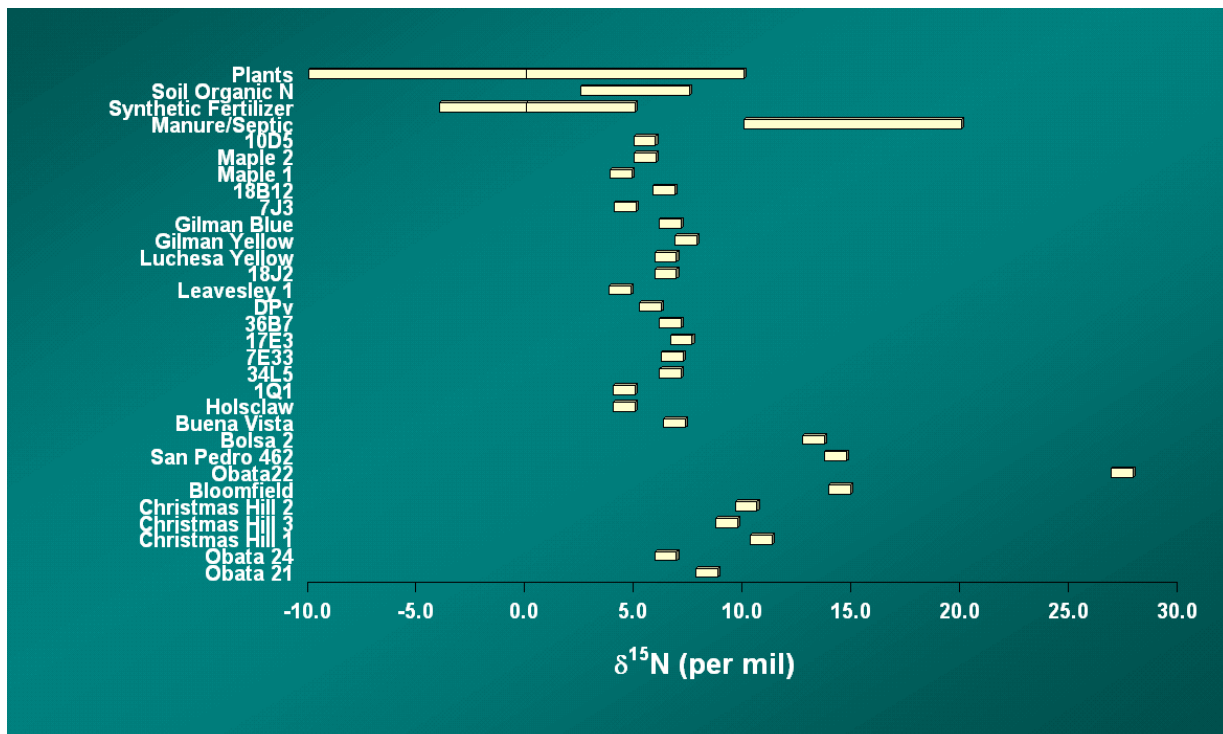


Figure 13. Bar graph shows the small range in $\delta^{15}\text{N}$ centered around +6‰ observed at most wells; wells in areas influenced by recycled water recharge have more positive values, due to denitrification.

Many of the wells with high $\delta^{15}\text{N}$ values also stand out as having high $\delta^{18}\text{O}$ (figure 14), suggesting some degree of denitrification. For example, Obata-22 shows a clear signal of denitrification, with extremely enriched $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values, a very low nitrate concentration of 1.3 mg/L, and being on a line of slope close to $\frac{1}{2}$ from Obata-21 (Figure 14). This denitrification has likely taken place during wastewater treatment, rather than in the aquifer, as excess nitrogen was not found.

A high $\delta^{15}\text{N}$ also distinguishes the San Pedro well (just adjacent to San Pedro Recharge Pond) from the majority of the results. Its accompanying high $\delta^{18}\text{O}$ nitrate, low dissolved oxygen concentration, and low nitrate concentration (1.2 mg/L) make it highly likely that this is another area affected by denitrification. (The similarly situated Church Pond wells had nitrate concentrations too low to carry out isotopic analyses. Furthermore, excess nitrogen from denitrification of only a few mg/L of nitrate would not be detectable.) As noted above, source waters in these areas have low starting nitrate concentrations, so denitrification near artificial recharge facilities is not expected to play a significant role in the overall fate of nitrate in the basin. A more extensive study near recharge facilities is necessary to determine whether these areas may be effective for long-term remediation.

For wells not influenced by recycled water or by recent artificial recharge, as described above, nitrate- $\delta^{15}\text{N}$ values fall in a narrow range. In particular, wells in this group with nitrate concentrations greater than 40 mg/L (11 of 27 wells) have nitrate- $\delta^{15}\text{N}$ values

between 3.8‰ and 6.6‰. This range is covered by reported ranges for mineralized inorganic fertilizers and soil organic N, but not by animal wastes or precipitation (Heaton, 1986; Townsend et al., 1994; Kendall, 1998). The wells most clearly affected by anthropogenic nitrate contamination (Holsclaw, Leavesley 1, Maple 1) have the lightest (most depleted) nitrogen isotope values (4.0‰, 3.8‰, and 3.9‰, respectively); solidly in the range expected for synthetic fertilizer. The most likely source of anthropogenic nitrate affecting groundwater concentrations is therefore inorganic fertilizer. Isotopic results do not support the possibility of a significant contribution from animal waste sources including septic and manure outside of areas under the influence of wastewater irrigation. While a significant component from soil organic nitrogen cannot be ruled out, the high concentrations observed are not consistent with results from previous studies in areas where soil nitrogen is the major source, which typically display nitrate concentrations in groundwater of less than 10 mg/L (Edmunds and Gaye, 1997; Williams et al., 1998).

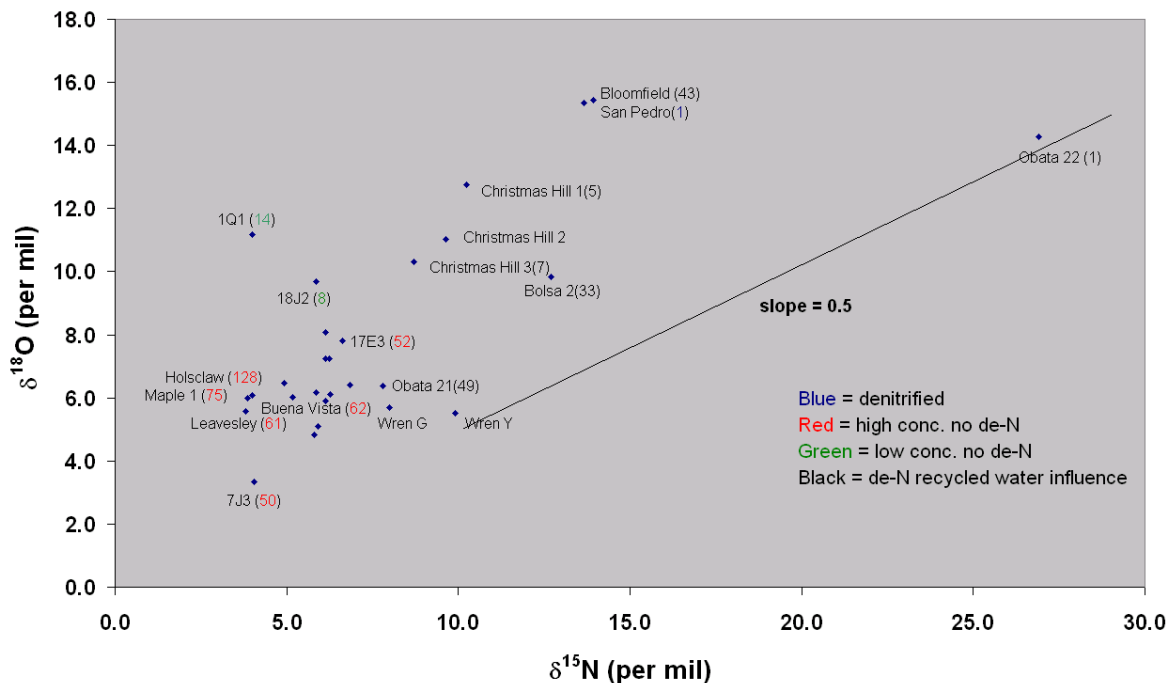


Figure 14. On a plot of $\delta^{15}\text{N}$ vs. $\delta^{18}\text{O}$ of nitrate, samples with residual nitrate from denitrification (which takes place at the wastewater treatment plant, before recharge) stand out from the majority of samples, for which fertilizer is the most likely source of N. Labels next to points are measured nitrate concentrations, color-coded according to the legend with the interpretation of possible denitrification.

As noted above, nitrate- $\delta^{18}\text{O}$ can be useful for distinguishing nitrate sources, especially if nitrate fertilizers are the main source, since they have an expected starting nitrate- $\delta^{18}\text{O}$ value of 23‰, the value for atmospheric oxygen. However, if ammonia fertilizer (rather than nitrate fertilizer) is applied and subsequently oxidized to nitrate, then one oxygen atom from air (at +23‰) and 2 from water (at roughly -6‰ for Llagas waters) combine to make up the nitrate-oxygen (Kendall, 1998). The resulting $\delta^{18}\text{O}$ -nitrate in that case

would be +3.6‰, a value somewhat lower than the observed values. Ammonium sulfate is commonly used for fertilization of tomatoes, peppers, and strawberries, major crops grown in the Gilroy area, and may be a major source of nitrate to groundwater. However, a contribution from nitrogen-fixing vegetation cannot be ruled out, and in a climate with a long dry season and soils that do not sustain significant denitrification, the observed nitrate- $\delta^{15}\text{N}$ and nitrate $\delta^{18}\text{O}$ values fall in the range expected for soil organic nitrogen as a natural nitrate source.

Inverse geochemical modeling calculations via PHREEQC were used to postulate mass transfer reactions that could explain the evolution of select water chemistry parameter values (pH, inferred HCO_3^- , Ca^{2+} , Mg^{2+}) in selected wells from the average chemical composition of reservoirs in the basin that could serve as potential sources of recharge. The allowed mass transfer reactions included NH_3 (as a nitrate source), CO_2 , calcite, and dolomite. CO_2 , which would be required in an inverse model to explain a water composition affected by mineralization of an animal waste discharge, is a required constituent in wells generally identified as being influenced by wastewater irrigation (figure 15), a finding that is consistent with the nitrogen isotope data.

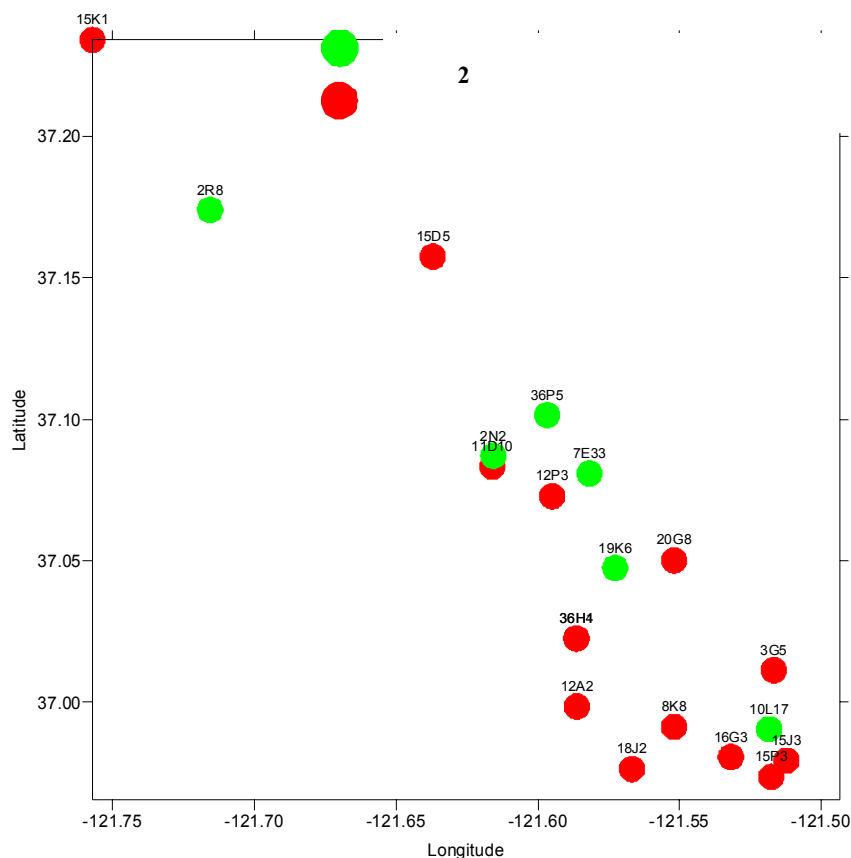


Figure 15. Required CO_2 input in inverse model calculations in select Llagas subbasin wells.

Among the major cations and anions, only magnesium appears to exhibit a discernable correlation with nitrate (figure 16), a feature that is presumably associated with the dissolution of dolomite and/or Mg-rich carbonate minerals. As dolomite is a common soil amendment, the pattern of dolomite distribution could, in principle, reveal clues to as to the distribution of nitrate fertilizer loading. The inverse modeling approach indicates that dolomite dissolution is a necessary component of the inverse models for a number of wells, with the highest values also located toward the southeast portion of the subbasin. This loose association with an animal waste signature in the area raises the possibility that much of the added dolomite simply reflects a natural mineralogical dissolution response of the aquifer material.

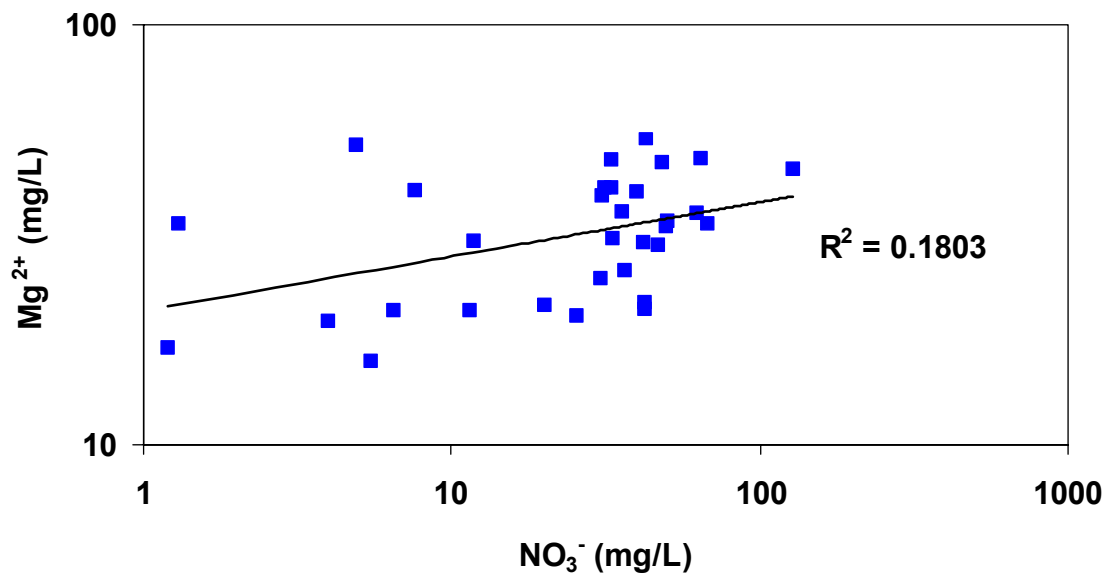


Figure 16. Observed magnesium concentrations versus nitrate in Llagas subbasin wells.

Effectiveness of Nitrate Management Program

As noted above, many of the educational and testing activities that make up the nitrate management program implemented by SCVWD began on a large scale in 2000 and later. Figure 17 shows the locations of 4 key growers that participated in the nitrate management assistance program beginning in January, 2000. Although some of the nitrate management activity took place at the sites shown, these growers have fields in multiple locations, with different crop rotations and different irrigation methods, which makes monitoring the effects of the activities difficult. Two wells, 36P5 and 10D5, are situated just downgradient from Grower B Farms (participated in the program) and Grower A (a major grower not listed as having participated in the program), respectively. The 36P5 well did have a reduction of 29% in its average nitrate concentration, from 59 mg/L (standard deviation 2.6, n=12), to 42 mg/L, as measured in 2003. The 10D5 well fluctuates widely (figure 8; mean concentration 82 mg/L standard deviation 49.8, n=14), but saw an increase above average summertime concentrations in the 2003 sampling.

Without first-encounter monitoring wells emplaced specifically near fields where changes have been instituted, more meaningful assessments based on well data cannot be determined.

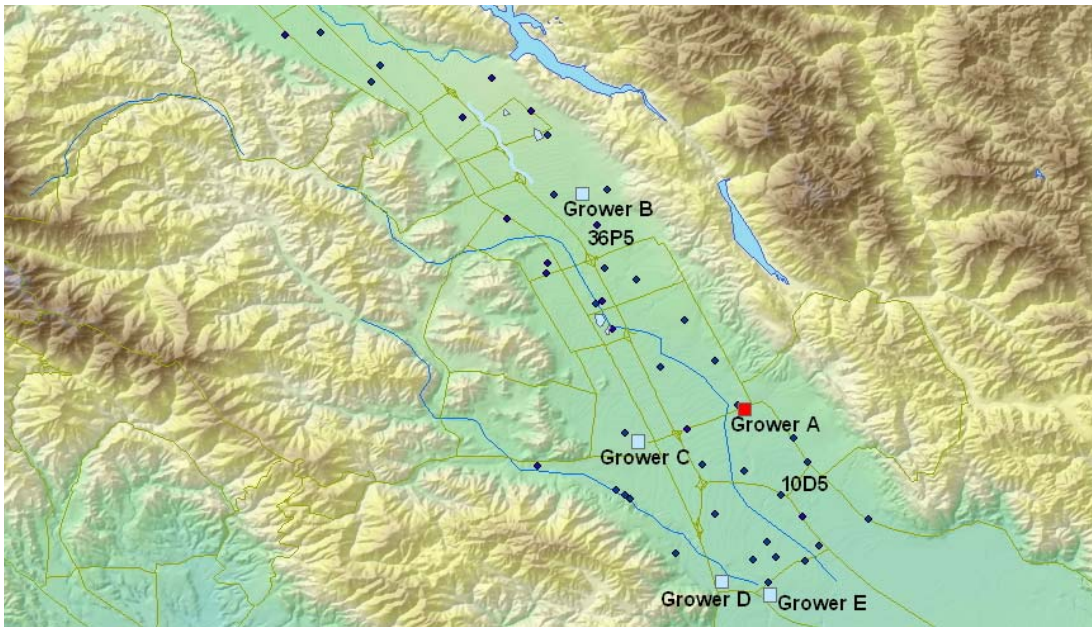


Figure 17. Four of the major growers (B through E) participating in the SCVWD nitrate management plan are shown with light blue symbols, along with one that did not (Grower A). Monitoring wells included in the study are not well situated to monitor changes in the flux of nitrate from those fields.

A more useful exercise for assessing the effect of the nitrate management activities on a regional scale is to examine nitrate patterns in wells with very young groundwater ages. Fourteen wells have calculated ages of less than 4 years, and as such record the most recent flux of nitrate to the saturated zone. Changes to the flux will be observed in these wells first. Of the fourteen wells with very young groundwater, 3 are just adjacent to artificial recharge ponds and have very low concentrations, as discussed above. Another 4 (Obata 22, Christmas Hill 1 and 2, and Bolsa2) are in areas receiving recycled water and have animal waste/denitrified signatures, as discussed above. Five of the remaining wells have low $\delta^{15}\text{N}$, indicating anthropogenic nitrate from fertilizer, and are in areas of high historical nitrate levels. Of these wells (Buena Vista-1, Holsclaw, Gilman Yellow, Luchessa Yellow, and Maple-1), 2 (Gilman Yellow and Holsclaw) had insignificant changes from mean concentrations of 1998-2000, 2 (Maple1 and Luchessa Yellow) had significant increases, and only one (Buena Vista-1) had a significant decrease. Groundwater age analyses indicate that the nitrate management plan has not yet resulted in a decrease in the flux of nitrate to the shallow aquifer in the areas tested.

Conclusions and Recommendations:

Inorganic fertilizer is almost certainly the main source of nitrate to shallow groundwater in the Llagas subbasin, so continued efforts to minimize application of fertilizer that is not taken up by plants but rather leached to groundwater is critical. The chemical form of nitrogen in fertilizer, the timing of application, and the method and timing of irrigation are important factors in the propensity for leaching of nitrate from soils. In particular, more efficient irrigation would minimize the chance that significant return flow of high nitrate groundwater leads to continued contamination of wells.

Assessing the effectiveness of the nitrate management program would benefit from installation or identification and testing of first-encounter wells that are just downgradient of fields where the plan is being carried out and where high contamination and young groundwater have been identified. Fields within ½ mile of Leavesley W-1, Holsclaw W-1, or Buena Vista W-1 would be good candidates if growers are participating in the program. Future work ought to include testing the competing hypotheses of contributions to the shallow aquifer from leaching of stored nitrate in the vadose zone, versus enhanced leaching of recently applied nitrate by late season irrigation. This could take the form of a relatively simple study in which vadose zone core samples are leached to determine the nitrate inventory in soil and unsaturated sediment in a few key areas of irrigated agriculture.

Saturated zone denitrification under fields and developed areas is not a significant process for the fate of nitrate, probably because of low organic carbon loading. Artificial recharge brings low nitrate water and may set up conditions necessary for denitrification – enhanced artificial recharge and shallow zone pumping could be used as a long term remediation strategy. A large portion of the shallow aquifer is highly vulnerable to contamination (of any non-reactive constituent), as evidenced by the widespread occurrence of very recently recharged groundwater (see also Moran et al., 2004). To the extent possible, reduction in sources over the large area where groundwater ages are less than 10 years is the optimal scenario for solving the contamination problem in the long term. Areas of lower groundwater vulnerability are to the east of Madrone Channel in Morgan Hill, and the southeastern-most portion of the subbasin in Gilroy. Only deep screened wells in the confined (southern) portion of the subbasin can be expected to be isolated from the input of nitrate for the next several decades. This area could be considered for future drinking water wells.

Acknowledgments

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Table 2a:

Location	LLNL ID	State Well ID	Well Name	Sample Collection	Elevation	Total Well Depth	Perf Top	Temp	Cond	pH	Field DO
						(ft bgs)	(ft bgs)	(°C)	(μS)		(mg/L)
Morgan Hill	101665	09S/02E-01Q01 M	1Q1	20030617	237.2	204	50	18.1	440	7.42	
Gilroy	101666	10S/04E-34L05 M	34L5	20030617	199.2	163	90	17.8	746	6.95	
San Martin	101667	10S/04E-17E03 M	17E3	20030617	252.7	200	180	19.5	500	7.27	
San Martin	101668	09S/03E-36B07 M	36B7	20030617	319.2	225	165	19.4	960	7.25	
Gilroy	101669	11S/04E-05C06 M	GILMAN YELLOW	20030617	134.6	305	247	19.6	472	7.47	8.0
Gilroy	101670	11S/04E-05C05 M	GILMAN BLUE	20030617	134.6	435	390	na	na	na	5.0
Gilroy	101671	11S/04E-05C04 M	GILMAN GREEN	20030617	134.6	750	655	22.7	366	8.37	<1
Gilroy	101672	11S/04E-05C03 M	GILMAN RED	20030617	134.6	880	840	22.9	1180	8.06	<1
San Martin	101673	09S/03E-07J03 M	7J3	20030618	314.3	230	130	18.5	634	7.48	
San Martin	101674	09S/03E-18B12 M	18B12	20030618	278.9	84	69	19.3	490	7.35	
San Martin	101675	09S/03E-35C12 M	MAPLE 1	20030618	305.1	61	48	18.9	657	7.06	
San Martin	101676	09S/03E-35C11 M	MAPLE 2	20030618	305.1	91	81	19.0	615	7.39	
Gilroy	101741	11S/04E-10D05 M	10D5	20030618	112.9	325	300				
Gilroy	101766	11S/04E-16K01 M	MW-21 OBATA FARMS	20030819	134.4	41	20	16.8	1020	6.82	
Gilroy	101767	11S/04E-15M02 M	MW-22 OBATA FARMS	20030819	144.6	40	10	17.9	1040	6.75	
Gilroy	101768	11S/04E-16G03 M	MW-24 OBATA FARMS	20030819	149.9	120	100	19.1	920	7.22	
Gilroy	101769	11S/03E-01Q02 M	CHRISTMAS HILL W-1	20030819	169.3	44	29				
Gilroy	101770	11S/03E-12A02 M	CHRISTMAS HILL W-2	20030819	168.0	44	29	19.1	458	7.03	
Gilroy	101772	11S/03E-12A03 M	CHRISTMAS HILL W-3	20030819	158.1	44	29	18.9	570	6.82	
Gilroy	101773	11S/04E-21G03 M	BOLSA W-2	20030820		91	70	18.3	990	6.89	
Gilroy	101774	11S/04E-15J03 M	BLOOMFIELD W-1	20030820		53	48	18.7	910	7.39	
Gilroy	101825	11S/04E-03G05 M	3G5	20031113	183.4	86	70	17.1	907	6.95	
Gilroy	101826	11S/04E-04F07 M	HOLSCLAW W-1	20031113	176.4	55	40	18.1	913	6.90	7.0
Gilroy	101827	10S/04E-20G08 M	BUENA VISTA W-1	20031113	240.8	90	80	19.5	892	6.92	8.0
San Martin	101828	10S/03E-13D08 M	CHURCH 452	20031113	249.3	46	26	19.8	407	7.13	<1
Morgan Hill	101829	09S/03E-23L05 M	SAN PEDRO 462	20031113	350.4	25	10	21.7	456	7.53	
Gilroy	101830	10S/03E-36H04 M	WREN-YELLOW	20031117	207.3	95	60	18.5	808	6.73	4.0
Gilroy	101831	10S/03E-36H03 M	WREN-BLUE	20031117	207.3	174	134	18.3	645	7.28	7.0
Gilroy	101832	10S/03E-36H01 M	WREN-GREEN	20031117	207.3	260	220	18.7	633	7.01	7.0
Gilroy	101833	10S/03E-36H02 M	WREN-RED	20031117	207.3	440	400	20.8	651	7.31	<1

Temp = temperature, Cond = electrical conductivity, DO = dissolved oxygen

Table 2a: con'd

Location	LLNL ID	State Well ID	Well Name	Sample Collection	Elevation	Total Well Depth	Perf Top	Temp	Cond	pH	Field DO
				yyyymmdd	<i>Ft msl</i>	<i>(ft bgs)</i>	<i>(ft bgs)</i>	(°C)	(μS)		(mg/L)
Gilroy	101834	11S/04E-08K08 M	LUCHESSA-YELLOW	20031117	161.2	103	48	17.9	766	7.02	7.0
Gilroy	101835	11S/04E-08K07 M	LUCHESSA-GREEN	20031117	161.2	452	397	17.8	308	9.96	<1
Gilroy	101836	11S/04E-08K06 M	LUCHESSA-RED	20031117	161.2	865	790	17.6	1720	9.66	<1
Gilroy	101837	10S/04E-28M05 M	LEAVESLEY W-1	20031117	193.1	60	50	18.7	929	7.20	5.0
San Martin	101838	10S/04E-07E33 M	7E33	20031119	254.6	228	180	17.6	585	7.40	
San Martin	101839	10S/03E-12C06 M	12C6	20031119	250	206	140	15.8	575	7.58	
Gilroy	101840	10S/04E-19K06 M	19K6	20031119	221.2	295	175	18.0	541	7.57	
Gilroy	101841	11S/04E-11J07 M	11J7	20031119	165.8	230	120	19.7	854	7.68	
Gilroy	101842	11S/04E-15P03 M	15P3	20031119	167.6			18.0	744	7.63	
Gilroy	101843	11S/04E-18J02 M	18J2	20031119	176.8	170	100	18.7	962	7.60	
Gilroy	101844	11S/03E-02E01 M	2E1	20031119	229.7	100	60	16.0	415	7.51	
San Martin	101845	10S/03E-12P03 M	12P3	20031119	238.2	182	100	17.5	527	7.41	
Gilroy	101846	10S/04E-32E06 M	LEAVESLEY YELLOW	20031120	197.8	285	225	18.3	514	7.37	6.0
Gilroy	101847	10S/04E-32E05 M	LEAVESLEY BLUE	20031120	197.8	395	350	19.2	485	7.42	6.0
Gilroy	101848	10S/04E-32E04 M	LEAVESLEY GREEN	20031120	197.8	616	560	18.7	380	9.10	<1
Gilroy	101849	10S/04E-32E07 M	LEAVESLEY RED	20031120	197.8	949	890	19.4	1350	11.22	<1
Coyote	101850	08S/02E-15K01 M	COYOTE NARROWS 1	20031215	203.4	220	195	18.2	626	7.33	3.0
Gilroy	101851	09S/03E-36P05 M	36P5	20031120	287	203	100	18.3	605	7.80	8.0
Gilroy	101852	09S/03E-34P01 M	34P1	20031120	296.7	163	103	18.2	661	7.17	9.0
Gilroy	101853	09S/03E-21C03 M	21C3	20031120	315.9	200	100	16.4	505	7.71	
Morgan Hill	101854	09S/02E-02R08 M	2R8	20031215	272.3	220	50	16.8	712	7.08	6.0
Morgan Hill	101855	09S/03E-15D05 M	COYOTE PUMP STATION	20031215	246.1	46	10	18.8	616	7.15	7.0
San Martin	101856	10S/03E-13K10 M	CHURCH 457	20031215	255.9	50	25	19.7	379	7.29	1.0
San Martin	101857	10S/03E-02N02 M	2N2	20031215	303.8	215		18.1	586	7.19	6.0
San Martin	101858	10S/03E-11D10 M	11D10	20031216	303.8	181	80	17.0	575	6.91	7.0
San Martin	101859	11S/04E-10L17 M	10L17	20031216	223.8	150			17	8.25	7.2
San Martin	101860	09S/03E-36B07 M	36B7	20031216	319.2	225	165				

Temp = temperature, Cond = electrical conductivity, DO = dissolved oxygen

Table 2b:

LLNL ID	$\delta^{18}\text{O}_{\text{SMOW}}$ in water	$\delta\text{D}_{\text{SMOW}}$ in water	$\delta^{15}\text{N}$ in nitrate	$\delta^{18}\text{O}$ in nitrate	Chloride	Nitrate	Sulfate	N_2	O_2	Ar
	(‰)	(‰)	(‰)	(‰)	(mg/L)	(mg/L)	(mg/L)	($\text{cm}^3\text{STP/g}$)	($\text{cm}^3\text{STP/g}$)	($\text{cm}^3\text{STP/g}$)
101665	-6.7		4.0	11.2	34.0	13.7	42.6	1.85E-02	5.13E-03	4.45E-04
101666	-6.2		6.1	7.3	83.8	109.0	51.0	2.21E-02	6.32E-03	5.29E-04
101667	-6.3		6.6	7.8	63.5	52.4	23.6	1.75E-02	6.11E-03	4.38E-04
101668	-6.1		6.1	8.1	102.5	43.5	20.7	2.16E-02	6.32E-03	5.19E-04
101669	-6.0		6.8	6.4	29.4	36.7	41.7	2.16E-02	4.69E-03	5.03E-04
101670	-6.1		6.1	5.9	25.7	34.7	29.4	2.12E-02	4.95E-03	5.07E-04
101671	-7.4				50.7	0.0	30.1	1.51E-02	3.22E-03	3.61E-04
101672	-7.5				491.8	0.0	17.7	1.95E-02	1.11E-03	4.31E-04
101673	-6.3		4.0	3.4	26.4	49.7	51.0	1.89E-02	7.24E-03	4.54E-04
101674	-6.5		5.8	4.8	18.3	28.2	27.3	1.87E-02	4.37E-03	4.52E-04
101675	-7.4		3.9	6.0	57.2	74.9	53.3	1.57E-02	6.09E-03	3.79E-04
101676	-7.4		4.9	6.5	56.2	47.5	45.8	2.00E-02	7.18E-03	4.71E-04
101741										
101766	-5.6		7.8	6.4	149.8	49.3	76.9	2.34E-02	3.09E-03	5.34E-04
101767	-4.9		26.9	14.3	177.0	1.3	114.5	3.00E-02	1.35E-03	6.12E-04
101768	-5.6		5.9	6.2	41.9	33.3	55.1	2.54E-02	3.21E-03	5.28E-04
101769	-5.5		10.3	12.8	17.1	4.6	29.6	2.00E-02	3.12E-03	4.50E-04
101770	-5.3		9.6	11.0	26.7	5.5	32.6	2.23E-02	2.49E-03	5.25E-04
101772	-5.4		8.7	10.3	45.9	6.5	54.2	2.08E-02	2.78E-03	4.90E-04
101773	-5.4		12.7	9.8	157.5	32.8	87.6	3.43E-02	1.31E-03	7.58E-04
101774	-5.8		13.9	15.4	57.1	42.5	120.7	3.49E-02	1.90E-03	5.94E-04
101825	-6.2				47.4	39.7	32.8	2.41E-02	5.05E-05	4.79E-04
101826	-5.8		4.0	6.1	35.2	128.0	73.9	1.50E-02	4.96E-03	3.58E-04
101827	-6.0		6.3	6.1	57.4	62.0	59.1	1.42E-02	5.25E-03	3.33E-04
101828	-4.1				9.3	0.0	15.9	1.55E-02	1.13E-04	3.70E-04
101829	-8.0		13.7	15.4	58.6	1.2	38.1	1.44E-02	1.41E-03	3.44E-04
101830	-5.7		9.9	5.5	44.4	30.8	63.0			
101831	-5.9				34.8	46.5	37.2			
101832	-5.7		8.0	5.7	32.5	36.2	35.4	2.08E-02	4.36E-03	4.54E-04

Table 2b: (con'd)

LLNL ID	$\delta^{18}\text{O}_{\text{SMOW}}$ in water	$\delta\text{D}_{\text{SMOW}}$ in water	$\delta^{15}\text{N}$ in nitrate	$\delta^{18}\text{O}$ in nitrate	Chloride	Nitrate	Sulfate	N_2	O_2	Ar
	(‰)	(‰)	(‰)	(‰)	(mg/L)	(mg/L)	(mg/L)	(%)	(%)	(%)
101833	-5.8		13.4		35.5	40.3	56.4	2.68E-02	1.63E-03	4.92E-04
101834	-6.0	-40	5.9	5.1	17.0	50.0	61.2	2.12E-02	4.78E-03	4.54E-04
101835	-6.7	-44			25.3	0.0	46.6	2.03E-02	2.57E-03	4.45E-04
101836	-6.9	-46			722.9	0.1	1.0	4.09E-02	6.30E-04	4.97E-04
101837	-5.9		3.8	5.6	19.6	60.5	31.4	2.05E-02	3.71E-03	4.52E-04
101838	-6.5	-45	6.2	7.2	40.6	42.1	39.8	2.06E-02	5.42E-03	4.69E-04
101839	-7.1	-51			47.5	30.5	41.4	1.93E-02	5.15E-03	4.28E-04
101840	-6.0		5.2	6.0	30.0	25.3	34.1	2.17E-02	5.21E-03	4.72E-04
101841	-6.4				46.5	0.0	42.1	2.06E-02	1.18E-03	4.23E-04
101842	-5.8				26.0	41.6	65.8	1.76E-02	5.52E-03	3.96E-04
101843	-6.3		5.9	9.7	89.8	7.6	87.5	2.00E-02	8.04E-04	4.45E-04
101844	-5.6				10.6	11.5	32.9	1.37E-02	2.08E-03	3.45E-04
101845	-5.2	-36			6.9	11.8	17.3	2.06E-02	2.89E-03	4.39E-04
101846	-5.6	-41			19.1	20.1	29.5	2.65E-02	4.38E-03	5.51E-04
101847	-6.0	-41	Insuff NO_3	Insuff NO_3	0.3	1.0	0.2	2.45E-02	4.53E-03	5.22E-04
101848	-6.4	-44	Insuff NO_3	Insuff NO_3	0.4	0.4	0.5	2.22E-02	7.68E-04	4.60E-04
101849	-7.2	-52	Insuff NO_3	Insuff NO_3	409.8	0.1	3.9	2.79E-02	9.98E-04	5.46E-04
101850	-5.6	-45			23.9	4.9	29.8	1.58E-02	2.10E-03	3.76E-04
101851	-6.5	-46			46.8	42.1	39.4	2.59E-02	7.02E-03	5.63E-04
101852	-6.0	-41			45.2	67.6	50.3	2.22E-02	6.56E-03	4.94E-04
101853	-9.0	-67			72.1	4.0	39.7	2.30E-02	5.62E-03	4.89E-04
101854	-6.3	-45			39.5	64.3	47.5	1.61E-02	3.30E-03	3.74E-04
101855	-6.7	-50			33.6	32.8	48.5	1.32E-02	5.56E-03	3.33E-04
101856	-2.8	-24			7.5	0.4		1.70E-02	5.97E-04	3.90E-04
101857	-6.1	-43			42.0	31.2	27.8	2.25E-02	4.75E-03	4.74E-04
101858	-5.8	-44			40.7	35.6	29.6	2.15E-02	5.64E-03	4.52E-04
101859	-6.1	-43			30.8	48.2	56.5	2.15E-02	1.72E-03	4.45E-04
101860	-5.6	-40			117.5	44.6	82.6	2.18E-02	2.31E-03	4.73E-04

Table 2c:

LLNL ID	Tritium	Tritium error	Excess Air	⁴ He radiogenic	Radiogenic Age	Percent pre-modern	Recharge Temp	Recharge Temp error
	(pCi/L)	(pCi/L)	(ccSTP/g)	(ccSTP/g)		(%)	(°C)	(°C)
101665	14.9	0.76	7.36E-03	<1E-10	15.9	0.44	15.4	1.4
101666	11.1	0.61	1.37E-02	1.8E-10	16.0	0.59	11.2	1.7
101667	11.1	0.61	1.84E-02	<1E-10	15.2	0.57	16.8	2.7
101668	2.7	0.34	1.58E-02	<1E-10	23.9	0.94	17.2	2.4
101669	12.4	0.67	1.13E-02	8.49E-09	0.6	0.55	16.5	1.8
101670	4.9	0.39	1.39E-02	4.34E-09	34.0	0.96	17.1	2.2
101671	0.5	0.22	3.65E-03	4.37E-07			11.9	1
101672	0.0	0.16	4.49E-03	7.55E-07	180.1*	1.00	10.8	1
101673	15.6	2.3	1.44E-02	1.22E-06			15.7	2.1
101674	11.7	1.58	1.11E-02	2.03E-08	11.3	0.50		
101675	10.9	0.54	4.74E-03	1.49E-09	3.9	0.56	15.4	1.2
101676	10.1	0.51	1.06E-02	1.28E-09	9.9	0.57	18.3	1.9
101741	11.9	0.59	2.51E-02	<1E-10	38.5	0.93	18.7	3.8
101766	19.7	1.61	7.33E-03	1.15E-07	66.7*		14.4	1.3
101767	13.7	0.72	5.69E-03	<1E-10	2.8	0.47		
101768	13.8	0.69	1.04E-02	<1E-10	15.6	0.48	14.1	1.6
101769	10.0	0.51	3.03E-03	6.92E-10	0.0	0.65	15.9	1.1
101770	13.2	0.63	3.87E-03	<1E-10	<1		13.7	1.1
101772	9.4	0.47	4.05E-03	<1E-10	16.9	0.67	13.8	1.1
101773	12.7	0.6	8.67E-03	<1E-10	2.4	0.51	15.5	1.5
101774	7.0	0.39	4.15E-03	<1E-10	26.6	0.88	14.6	1.1
101825	2.2	0.18	1.57E-02	<1E-10	28.9	0.97	16.9	2.4
101826	11.9	0.49	2.50E-03	<1E-10	3.9	0.52	14.9	1
101827	6.4	0.31	2.26E-03	2.73E-10	<1		17.8	1
101828	10.7	0.44	4.50E-03	<1E-10	<1		12.0	1
101829	11.2	0.45	2.51E-03	<1E-10	<1		16.9	1
101830	11.4	0.5	6.76E-03	1.11E-08			15.1	1.3
101831	8.8	0.43	1.54E-02	<1E-10	27.1	0.85	15.6	2.2
101832	3.9	0.24	1.25E-02	<1E-10	26.2	0.93	15.1	1.9
101833	8.2	0.39	1.27E-02	3.35E-08			14.2	1.8

Table 2c: (con'd)

LLNL ID	Tritium	Tritium error	Excess Air	⁴ He radiogenic	Radiogenic Age	Percent pre-modern	Recharge Temp	Recharge Temp error
	(pCi/L)	(pCi/L)	(ccSTP/g)	(ccSTP/g)		(%)	(°C)	(°C)
101834	12.5	1.39	1.02E-02	<1E-10	2.6	0.52	14.9	1.6
101835	-0.3	0.73				1.00		
101836	2.3	1.05	1.00E-02	5.71E-06	163.9*	1.00	7.8	1.2
101837	12.7	0.52	1.12E-02	<1E-10	6.3	0.46	15.0	1.7
101838	10.6	0.46	1.40E-02	<1E-10	22.1	0.73		
101839	11.3	0.46	1.26E-02	<1E-10	10.9	0.52	15.9	2
101840	11.7	0.56	1.56E-02	<1E-10	23.5	0.73	16.0	2.3
101841	0.1	1.01						
101842	13.1	0.54	1.40E-02	<1E-10	27.2	0.78	15.0	2
101843	1.2	0.14	7.19E-03	7.62E-07			12.8	1.3
101844	8.5	0.44	1.25E-03	<1E-10	2.0	0.68	13.5	0.9
101845	11.1	0.48	1.27E-02	5.83E-10	12.4	0.54	15.7	1.9
101846	11.9	0.58	1.56E-02	<1E-10	25.8	0.77	14.5	2.2
101847	9.1	0.46	1.40E-02	<1E-10	28.9	0.87	15.1	2
101848	1.2	0.15	8.93E-03	4.8E-08				
101849	1.6	0.25	8.70E-03	1.3E-06	138.0*	1.00	8.9	1.2
101850	13.4	0.54	3.40E-03	<1E-10	9.3	0.42	17.0	0.8
101851	11.3	0.51	1.58E-02	<1E-10	20.3	0.67	16.0	2.3
101852	9.8	0.43	2.10E-02	<1E-10	20.6	0.72	15.9	2.9
101853	10.7	0.46	1.70E-02	<1E-10	6.8	0.55	17.3	2.6
101854	11.5	0.46	3.73E-03	1.33E-08	4.4	0.53	17.0	0.8
101855	10.1	0.42	4.26E-04	<1E-10	1.0	0.63	17.2	0.8
101856	12.4	0.48	4.97E-03	<1E-10	2.5	0.52	19.0	0.9
101857	10.9	0.45	1.36E-02	<1E-10	21.2	0.70	17.0	1.2
101858	11.4	0.46	2.20E-02	<1E-10	19.8	0.66	16.0	1.7
101859	6.1	0.26	6.69E-03	<1E-10	20.3	0.82	15.3	0.9
101860								

*Calculated age is useful only as an indicator of the presence of mantle helium

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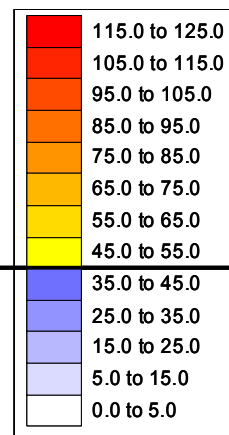


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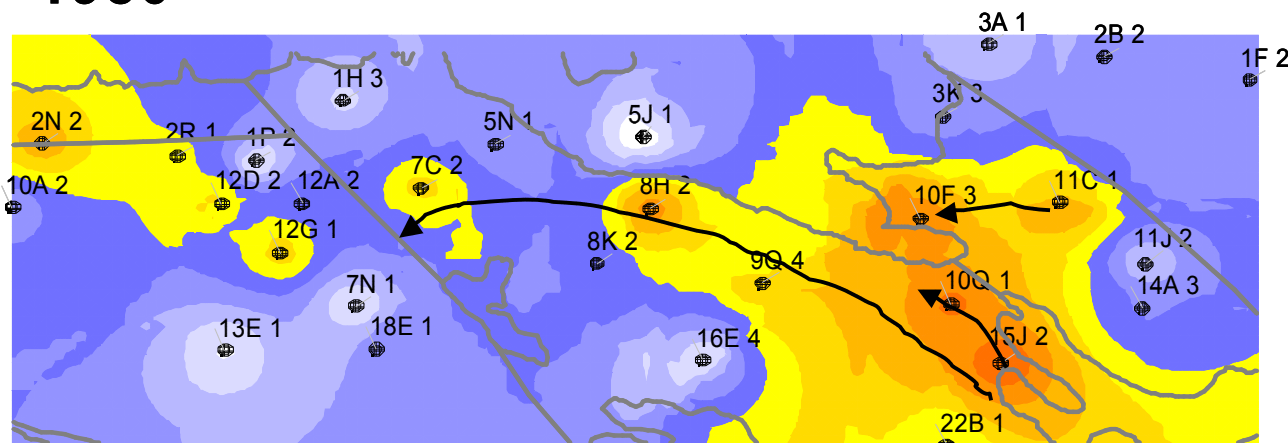
California GAMA Program: Sources and transport of nitrate in groundwater in the Livermore Valley Basin, California

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On the cover: Contoured nitrate concentrations (as NO_3^- in mg/L) in Livermore Valley groundwater from 1980 water quality data (data courtesy of Zone 7 Water Agency)

Sources and transport of nitrate in groundwater in the Livermore Valley Basin, California

Executive Summary

A critical component of the State Water Resource Control Board's Groundwater Ambient Monitoring and Assessment (GAMA) Program is to assess the major threats to groundwater resources that supply drinking water to Californians (Belitz et al., 2004). Nitrate concentrations approaching and greater than the maximum contaminant level (MCL) are impairing the viability of many groundwater basins as drinking water sources. Source attribution and nitrate fate and transport are therefore the focus of special studies under the GAMA program. This report presents results of a study of nitrate contamination in the aquifer beneath the City of Livermore, where high nitrate levels affect both public supply and private domestic wells.

Nitrate isotope data are effective in determining contaminant sources, especially when combined with other isotopic tracers such as stable isotopes of water and tritium-helium ages to give insight into the routes and timing of nitrate inputs to the flow system. This combination of techniques is demonstrated in Livermore, where it is determined that low nitrate reclaimed wastewater predominates in the northwest, while two flowpaths with distinct nitrate sources originate in the southeast. Along the eastern flowpath, $\delta^{15}\text{N}$ values greater than 10‰ indicate that animal waste is the primary source. Diminishing concentrations over time suggest that contamination results from historical land use practices. The other flowpath begins in an area where rapid recharge, primarily of low-nitrate imported water (identified by stable isotopes of water and a tritium-helium residence time of less than 1 year), mobilizes a significant local nitrate source, bringing groundwater concentrations above the MCL of $45 \text{ mg NO}_3 \text{ L}^{-1}$. In this area, artificial recharge of imported water via local arroyos induces flux of the contaminant to the regional aquifer. The low $\delta^{15}\text{N}$ value (3.1‰) in this location implicates synthetic fertilizer. Geochemical modeling supports the hypothesis of separate sources, one including organic carbon, as from animal waste, and one not. In addition to these anthropogenic sources, natural nitrate background levels between 15 and $20 \text{ mg NO}_3 \text{ L}^{-1}$ are found in deep wells with residence times greater than 50 years.

Introduction and Background

Nitrate contamination of California drinking water supplies is pervasive—about 10% of California public drinking water supply wells produce water that exceeds the regulatory drinking water limit, and a much larger fraction produce water which approaches the limit (CA DHS, 2004). Nitrate contamination of groundwater is a growing concern for drinking water supplies not just in California, but also in many areas in the United States. Between 1993 and 2000, the U.S. Geological Survey's National Water-Quality Assessment program found that 9% of domestic supply wells and 2% of public supply wells exceeded the Environmental Protection Agency's maximum contaminant level (MCL) for drinking water of $45 \text{ mg NO}_3 \text{ L}^{-1}$ (10 mg L^{-1} as N) (Nolan et al., 2002). The human activities that contribute nitrate to groundwater—animal operations, crop fertilization, wastewater treatment discharge, septic systems—are ongoing and essential to the industry and commerce of the State of California. Best management practices can mitigate source loading but not eliminate it. Furthermore, nitrate is expensive to remove from drinking water supplies, especially in public and

private systems that rely on untreated groundwater and do not have the necessary water treatment infrastructure. These factors combine to make nitrate the greatest contaminant threat to California's drinking water supply.

The ultimate goal of the *Groundwater Quality Monitoring Act of 2001* (AB599) is the implementation of a comprehensive monitoring program to allow groundwater basin assessment. Assessment is a broad term, but encompasses assessing susceptibility of groundwater to contamination, characterizing current water quality in a basin, and predicting future water quality under different conditions. Because of the potential threat that nitrate poses to drinking water supplies, special studies are focused on basin-scale nitrate contamination. To meet these goals, basin assessment must consider the current inventory of nitrate in basin soils and waters, current and past source loading, groundwater recharge and transport, and nitrogen cycling in the soil, vadose and saturated zone. Nitrate occurs naturally, has relatively low-intensity point, distributed and nonpoint sources, and has a long history of introduction into the environment. Surface nitrogen loading has dramatically increased in the last 50 years, making groundwater ages a useful approach to assessing historical inputs and to determining the effectiveness of relatively recently implemented nitrate management plans.

In many groundwater basins, urbanization has created a growing demand for drinking water, while long histories of agricultural activity have left aquifers potentially at risk from nitrate. Water agencies and regulators can develop more effective management strategies when nitrate sources are well understood. Many past studies have used ^{15}N and ^{18}O in nitrate as tracers of the source and fate of contamination (Kendall and Aravena, 2000). This dual isotope technique is sometimes limited by the overlap of source isotope values and by the variety of potential processes that affect nitrate (Aravena *et al.*, 1993; Mengis *et al.*, 2001). Successful studies of nitrate behavior and distribution must take into account the many environmental and historical factors that affect nitrate fate and transport (Bohlke and Denver, 1995).

Our purpose is to improve upon traditional nitrate investigation methods that often yield ambiguous interpretations. We apply an integrated analytical approach using multiple lines of evidence to resolve the manifold origins and pathways of nitrate contamination. This approach is demonstrated in Livermore, CA, a city that relies on groundwater for a significant portion of its drinking water, but where MCL exceedances have occurred at 6 of the 13 public supply wells in the contaminated portion of the basin. As in many regions where this approach may be beneficially applied, Livermore has a decades long history of varied nitrate inputs in a complex groundwater system.

Previous studies of Livermore's nitrate problem have estimated nitrate loading from various sources using literature ranges of potential nitrate inputs from these sources (Steinbergs and Wong, 1980; Raines, Melton, and Carella, Inc., 2002). These assessments consider only theoretical calculations of modern inputs and do not account for residual inputs or for the effects of hydrogeology. In our study, we incorporate these factors by interpreting nitrate isotope and concentration data in the context of local hydrogeology and land use history. We explore nitrate interactions along flowpaths using geochemical modeling and we analyze dissolved gases to determine whether saturated-zone denitrification has taken place. Additionally, other isotopic tracers such as stable isotopes of water and tritium-helium residence times give valuable insight into the routes and timing of various nitrate contributions to the flow system.

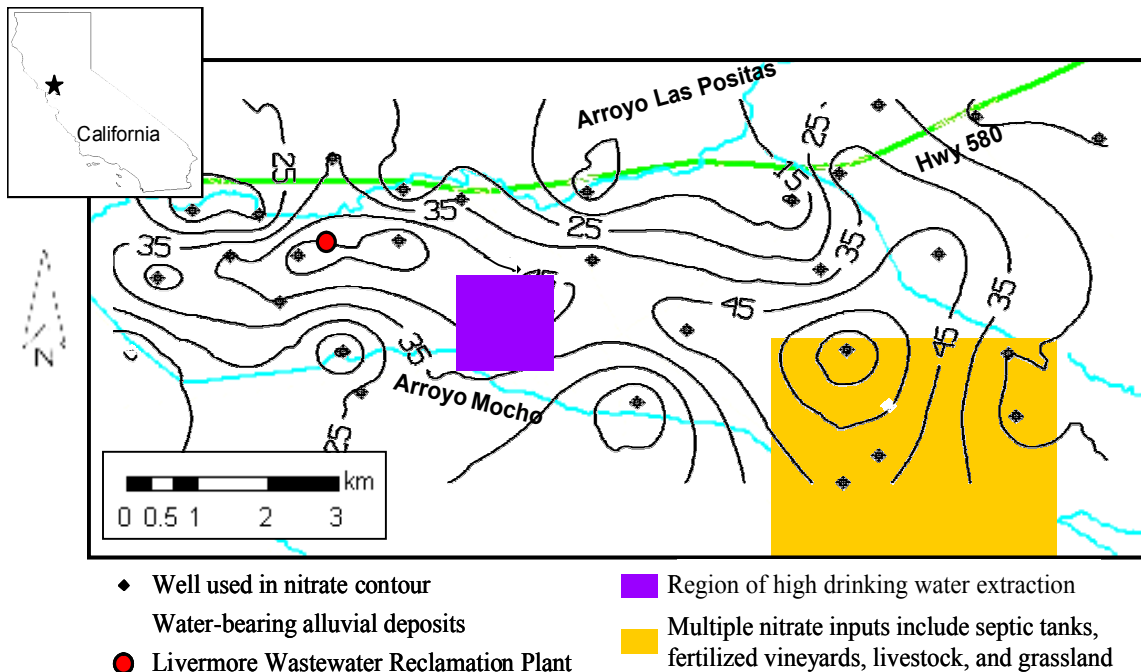


Figure 1. Nitrate concentrations in Livermore Valley. Approximate nitrate contours, in mg/L, kriged using RockWareTM. Wells used to draw contours have depths less than 35 m, the approximate depth of a non-continuous aquiclude and thus the defined cutoff for the aquifer's shallow zone. The apparent gap in the center of the map is an artifact of the limitations of the data, rather than a break in the plume.

This study demonstrates the application of an integrated analytical approach in a nitrate-impacted groundwater basin. Interpretation of nitrate ^{15}N and ^{18}O data to identify contamination sources is enhanced through the use of additional isotopic and chemical tracers. We use well water major ion analyses to delineate the extent of the high nitrate region, and use historical data, collected for nitrate monitoring purposes, to track concentration changes through time. Stable isotopes of water provide information about groundwater sources, and residence time methods using tritium and noble gas measurements further constrain the source history. Possible reactions of nitrate are accounted for by analysis of dissolved gases, which can indicate whether saturated-zone denitrification has taken place. The methods used here could be widely applied in the many groundwater basins where urbanization has created a greater demand for drinking water, and where decades of agricultural activity have left a potential source of nitrate to groundwater.

Site Description and Land Use History

Multiple potential nitrate sources in the Livermore Valley from both past and present land uses make it an ideal setting for a multi-tracer geochemistry approach. Nitrate monitoring programs identified two locations of particular concern as possible origins of contamination. Around the Livermore Wastewater Reclamation Plant (LWRP), treated wastewater is used in irrigation. In the 1980s, contributions from LWRP were identified as the cause of high levels of nitrate in groundwater in that area (Sylvester, 1983). Subsequently, wastewater treatment methods were upgraded to include a tertiary treatment step that induces denitrification and reduces nutrient concentrations considerably. In 2003, the average monthly nitrate concentration in the applied water was only 4.9 mg L^{-1} (pers. comm., D. Atkins).

The other area of concern is the unincorporated southeast region of the valley (Figure 1). Past monitoring data show that as early as 1980, a nitrate plume originating in this location extended at least to the area where most groundwater extraction for drinking water takes place (Figure 1 and cover figure; unpublished data, Zone 7, 2003). A number of possible nitrate contamination sources exist in the southeast. Several reports in the past have implicated septic leachate as a primary nitrate source (Sylvester, 1983; Sorenson *et al.*, 1984; Raines, Melton, and Carella, Inc., 2002). In this unsewered area, approximately 100 residences have septic systems, a number that has not changed significantly in the past 30 years (Raines, Melton, and Carella, Inc., 2002). Another possible source is livestock waste from both modern and historical inputs. For many decades, ending in the early 1970s, poultry farming was a significant operation in this area. Over the last century, various grazing operations have existed on the grassland to the south and east of this area (Raines, Melton, and Carella, Inc., 2002).

This southeast region also includes vineyards which have increased in acreage over the last several decades to the current area of approximately 8 km^2 (Raines, Melton, and Carella, Inc., 2002). Although vineyards tend to use less nitrogen fertilizer than vegetable crops, they can still contribute significant nitrate to groundwater. One recent report found groundwater nitrate concentrations of up to 61.6 mg L^{-1} beneath grape fields in the San Joaquin Valley, CA (Burow, *et al.*, 1998), while another demonstrated that, even with closely controlled drip irrigation, 67% to 79% of fertilizer nitrogen applied to vineyards in the spring remained in the soil at harvest time, available for leaching with winter rains (Hajrasuliha, 1998).

Another possible nitrate source in the valley is that formed from the oxidation of organic nitrogen, naturally found in soil as a result of plant decomposition and microbial activity (Kendall and Aravena, 2000). Natural nitrate concentrations in groundwater below temperate region grasslands, unimpacted by anthropogenic activities, are generally below 9 mg L^{-1} (Edmunds and Gaye, 1997). In arid and semiarid regions where denitrification is unlikely, however, greater amounts of natural nitrate can accumulate in soils and be available for leaching to groundwater (Edmunds and Gaye, 1997; Brenner *et al.*, 2001; Bohlke, 2001). In Livermore's climate and habitat, leguminous vegetation that supports nitrogen-fixing bacteria is an important potential nitrate source. Burr clover and vetch, species that produce between 90 and $200 \text{ kg ha}^{-1} \text{ y}^{-1}$ of nitrate (National Research Council, 2001), thrive in Livermore during warm, wet winters (Steinbergs and Wong, 1980). It is often assumed that nitrate produced by legumes is balanced by denitrification

(Steinbergs and Wong, 1980), but in Livermore's dry summer season, it is possible that there is not enough soil moisture to support denitrification of this large quantity of nitrate. A study in a North African region with a similar semiarid climate attributed groundwater nitrate levels as high as 250 mg L^{-1} to nitrogen fixed by legumes (Edmunds and Gaye, 1997).

METHODS

Sample Collection

The thirty-two well sampling locations are shown in Figure 2. At Zone 7, Las Positas Golf Course and LWRP monitoring wells, samples were taken using a portable submersible pump. At private domestic wells and California Water Service Company supply wells, dedicated well pumps were used. Most ion and isotope samples were filtered in the field with a $0.45\mu\text{m}$ in-line filter. Nitrate isotope samples were loaded onto anion exchange columns within 24 hours of sampling at LLNL, and ion analyses were performed within 48 hours of sampling. For excess nitrogen analyses, dissolved gases (nitrogen, oxygen, and argon) were collected in 40-mL vials (VWR TraceClean™, amber borosilicate; 0.125-inch septum liner) with no headspace. Samples were stored in coolers on ice and analyzed within 24 hours of sampling. A 1-L Pyrex bottle with a polypropylene plug seal cap was filled for tritium analysis and a 30-mL clear, French-square type glass bottle with a Qorpak™ polyseal-lined cap was filled for analysis of stable isotopes O and H in water. Approximately 10 mL of groundwater was collected in copper tubes pinched by metal clamps for noble gas samples.

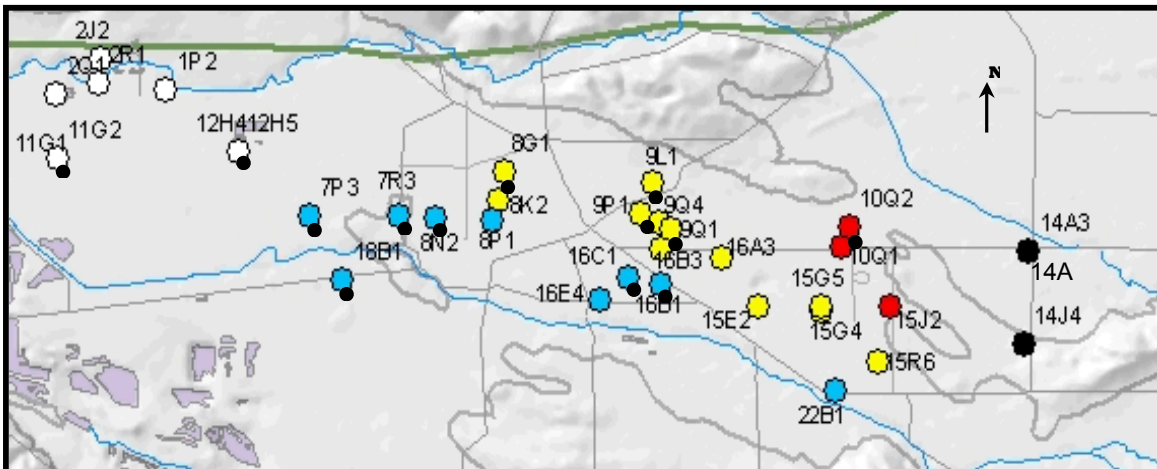


Figure 2. Map of the east side of the Livermore Basin showing wells sampled for the study. Color codings are related to geochemical and geographic groupings described in the text.

Laboratory Methods

Nitrate isotope samples were analyzed at the Environmental Isotopes Lab at the University of Waterloo, all other analyses were performed at LLNL. After extraction as silver nitrate, nitrogen gas for the measurement of $\delta^{15}\text{N}$ was produced by the sealed tube Cu/copper oxide method (Kendall and Grim, 1990; Flatt and Heemskerk, 1997) and CO_2 for measurement of $\delta^{18}\text{O}$ was produced by combustion with graphite. The isotope ratios of these gases were measured on a PRISM isotope ratio mass spectrometer. $\delta^{15}\text{N}$ results are reported as per mil relative to AIR and $\delta^{18}\text{O}$ results are referenced to VSMOW. Anions and cations were measured by ion chromatography on a Dionex IC DX-600 with a precision of $\pm 2.7\%$ relative standard deviation for nitrate. Oxygen isotopes of water were measured on a VG PRISM isotope ratio mass spectrometer. Results are reported as per mil with reference to VSMOW and have a precision of $\pm 0.1\%$. Deuterium was measured on the VG PRISM after extraction of hydrogen by the zinc reduction technique. Results are reported as per mil with reference to VSMOW and have a precision of $\pm 0.9\%$. Dissolved gases for examination of excess nitrogen were measured by membrane inlet mass spectrometry (MIMS) with an SRS RGA200 quadrupole mass spectrometer (Kana et al., 1994). ^3He and ^4He were measured on a VG5400 mass spectrometer, Ar was measured using a high-sensitivity capacitive manometer, and Ne, Kr, and Xe were measured on an SRS RGA200 quadrupole mass spectrometer. Tritium was determined by measuring the rate of ^3He accumulation. Residence time calculations were made by combining measurements of tritium with measurements of its decay product, ^3He , and excess air was determined from measured Ne concentrations. In this calculation, noble gas data was used to separate tritogenic helium from that from other sources (Ekwurzel, 2004).

Isotope and Dissolved Gas Techniques

A variety of nitrate fractionation processes lead to unique isotopic signatures for different nitrate sources. As a result, isotope values of nitrogen and oxygen can be useful in identifying the origin of groundwater nitrate (Figure 3). Synthetic fertilizers generally have $\delta^{15}\text{N}$ values between -2% and $+4\%$ (Kendall et al., 1998). By the time it reaches the groundwater, however, fertilizer nitrogen tends to be enriched by several per mil over the original source, often making it indistinguishable from soil organic nitrogen, which tends to have $\delta^{15}\text{N}$ values of $+3\%$ to $+8\%$ (Bohlke and Denver, 1995). Due to volatile loss of ammonia from manure, nitrate from animal waste has higher $\delta^{15}\text{N}$ values, usually greater than $+10\%$, and so can often be distinguished from other sources. All animals produce waste with similar $\delta^{15}\text{N}$ values, though, so isotopes alone are usually not useful in differentiating between septic waste and other animal wastes (Kendall, 1998; Choi et al., 2003).

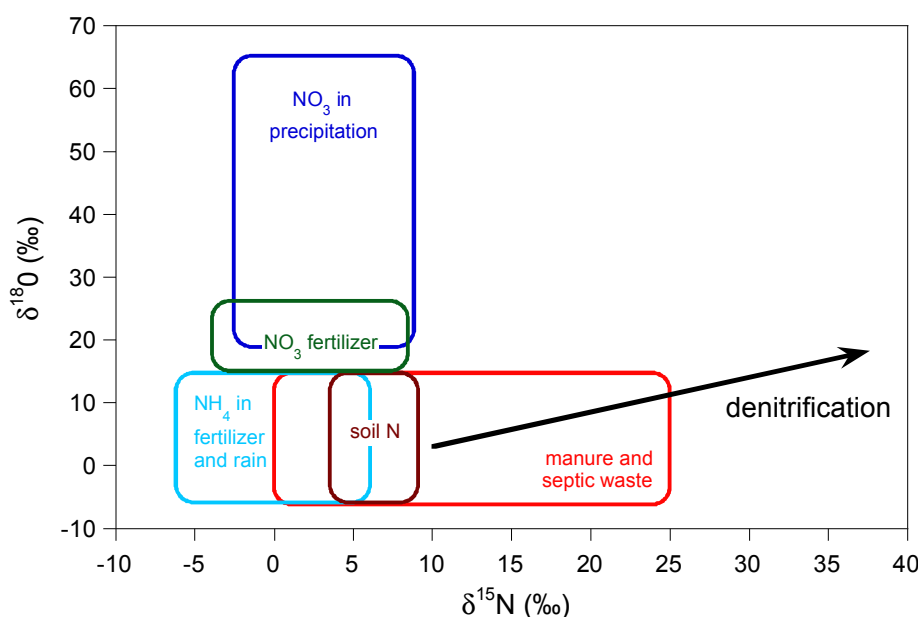


Figure 3: Isotopic composition of nitrogen and oxygen in nitrate from different sources (after Kendall, 1998).

Oxygen isotope values of nitrate can help clarify source identification, especially to separate nitrate fertilizer input from other sources, which produce nitrate by nitrification of ammonium or organic nitrogen. The $\delta^{18}\text{O}$ in nitrate fertilizers has a value close to the atmospheric value of +23‰. Other sources of nitrate incorporate two oxygen atoms from water and one from dissolved oxygen gas, leading to lighter $\delta^{18}\text{O}$ values dependent on the oxygen isotopes in the water (Kendall and Aravena, 2000). Nitrate from ammonium nitrate fertilizers will have $\delta^{18}\text{O}$ values that reflect both processes (Aravena et al., 1993).

Nitrate isotope data are also valuable as indicators of the occurrence of denitrification; as denitrification occurs, nitrogen and oxygen in nitrate are enriched in a characteristic 2:1 ratio (Kendall, 1998). Saturated zone denitrification can also be identified by the presence of its end product, excess nitrogen, dissolved in groundwater. Atmospheric nitrogen is distinguished from excess nitrogen by comparison with dissolved argon, the dominant source of which is atmospheric (Kana et al., 1994; Vogel et al., 1981). We employ both methods to check for possible denitrification.

Geochemical Modeling

Geochemical modeling was carried out using the inverse modeling capabilities of the U.S. Geological Survey's PHREEQC geochemical model (Parkhurst and Appelo, 2002) to identify interphase mass transfer reactions that reconcile elemental mass balances and charge balances in representative nitrate-impacted and background groundwater compositions (major cations, anions, and pH) along both the manure flowpath and the alluvial channel flowpath (Figure 4).

2000

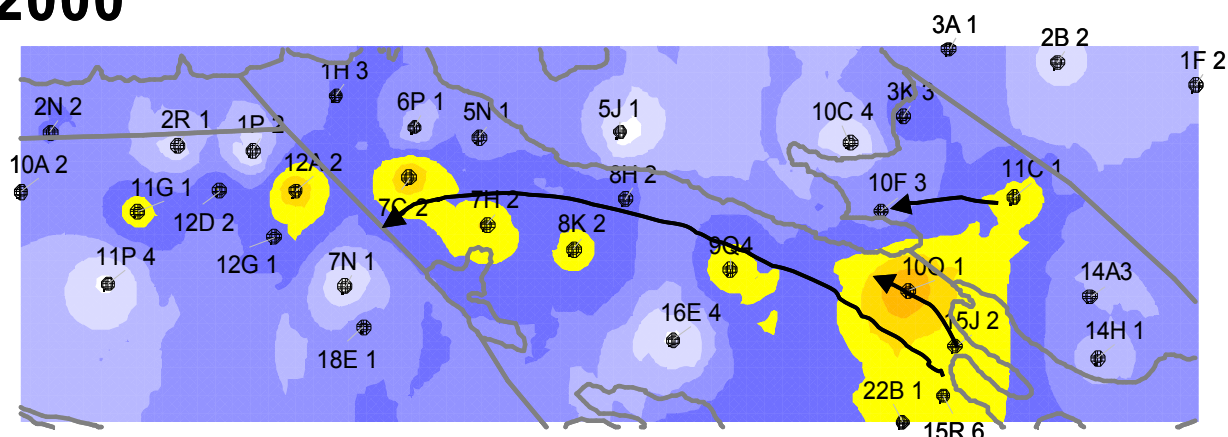


Figure 4. Nitrate contours drawn from the extensive, historical water quality dataset from Zone 7 (data shown are from 2000). Arrows indicate flowpaths discussed in the text.

The first step in implementing such an inverse modeling approach is the definition of contaminant-free and maximally contaminant-impacted end-member water compositions for each flowpath. Ideally, this is accomplished via extrapolation of best-fit linear relationships between geochemical parameter values and corresponding nitrate concentrations using all historical data from all wells along a flowpath. The parameter values associated with the estimated nitrate background (15 mg L^{-1}) and the nitrate peak are then assigned to the idealized contaminant-free and maximally contaminant-impacted end-members.

This method was only possible for pH and cations along the manure flowpath. In the other, non-ideal situations, end-members were constructed based on the following assumptions. For anions along the manure flowpath, the historical low-nitrate measurement at the upgradient well was taken to represent the contaminant-free end-member, while the historical high-nitrate measurement from the downgradient well was used as the contaminant-impacted end-member.

Along the alluvial channel flowpath, groundwater is subject to multiple nitrate inputs and mixing processes, so modeling was limited to the initial portion of the flowpath. Well 16A3, a downgradient monitoring well located in the highest concentration part of the nitrate plume, and for which historical data were available, was used to establish the maximally contaminant-impacted end-member. Because most parameters at this location were relatively stable, end-member values were based on averaged rather than extrapolated data. Due to the severity of the contamination along this flowpath, none of the historical data were acceptable to represent a nitrate-free end-member. Instead, two non-plume wells with environmental characteristics similar to those of the flowpath's source region were selected as surrogates for the upgradient well. Data from these wells were extrapolated to determine the contaminant-free end-member.

Historical averages of parameters at a deep, tritium-dead well and from an SBA monitoring station were estimated as potential inputs from these water sources. While these water compositions do not represent true collinear end-members along groundwater flowpaths, they do represent contrasting water compositions for each of the respective

flowpaths that presumably integrate the effects of the geochemical processes associated with nitrate loading. Putative phases involved in the mass transfer reactions include a nitrogen source (NH_3); organic carbon associated with animal fertilizer or septic tank leachate (idealized as CH_2O); carbonate minerals CaCO_3 and dolomite ($\text{CaMg}(\text{CO}_3)_2$); possible soil amendments dolomite, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and KCl ; ion exchangers (NaX , KX , MgX_2 , CaX_2); and O_2 , required to oxidize both NH_3 and CH_2O . These phases were selected for the PHREEQC inverse model with the added constraints that NH_3 , CH_2O , gypsum, KCl , and O_2 could only be utilized as reactants, not products. The same constraint was placed on dolomite, $\text{CaMg}(\text{CO}_3)_2$, as its precipitation kinetics are regarded as extremely slow (Morse and Mackenzie, 1990).

RESULTS AND DISCUSSION

Nitrate-source data is most successfully interpreted in the context of the constraints that can be placed on the groundwater flow system using conventional hydrogeological data along with other isotopic and geochemical tracers. Nitrate concentrations are highest in the southeast part of the study area, where many of the wells exceed the MCL (Table 1). The contamination extends to the area of major groundwater extraction as shown in the contour map in Figure 1. In conjunction with the estimated flowpaths, this supports the conclusion of past studies that the most significant nitrate contamination originates in the southeastern recharge area. Current and historical data consistently record higher nitrate concentrations in shallow monitoring wells than in deep wells, suggesting a plume with a shallow core. Nitrate concentrations identify the problem regions but are not diagnostic for distinguishing among competing sources or for helping identify historic or contemporary land use practice culpability. The following methods are used to identify nitrate source(s), to examine in detail the possibility of denitrification, and to delineate nitrate transport on the sub-basin scale.

Excess Nitrogen

The possibility of saturated zone denitrification must be considered before any conclusions can be drawn based on nitrate concentrations or nitrate isotope values. Samples for which noble gas data are available have recharge temperatures calculated to be between 11.8 and 21.6 C (Table 1). All nitrogen to argon ratios fall within the general range delineated for these temperatures by equilibrium solubilities and excess air trends, indicating that excess nitrogen is not present (Figure 5). Although these results do not exclude the possibility of denitrification before transport to the water table, they demonstrate that saturated zone denitrification is not an important process. This result is consistent with low dissolved organic carbon ($< 1.5 \text{ mg/L}$ $n=9$) and high dissolved oxygen concentrations that indicate an aerobic system with low reduction potential and lack of an electron donor. Groundwater nitrate data, therefore, may be interpreted directly as indicative of nitrate source, without accounting for attenuation or isotopic enrichment due to denitrification along the flowpath.

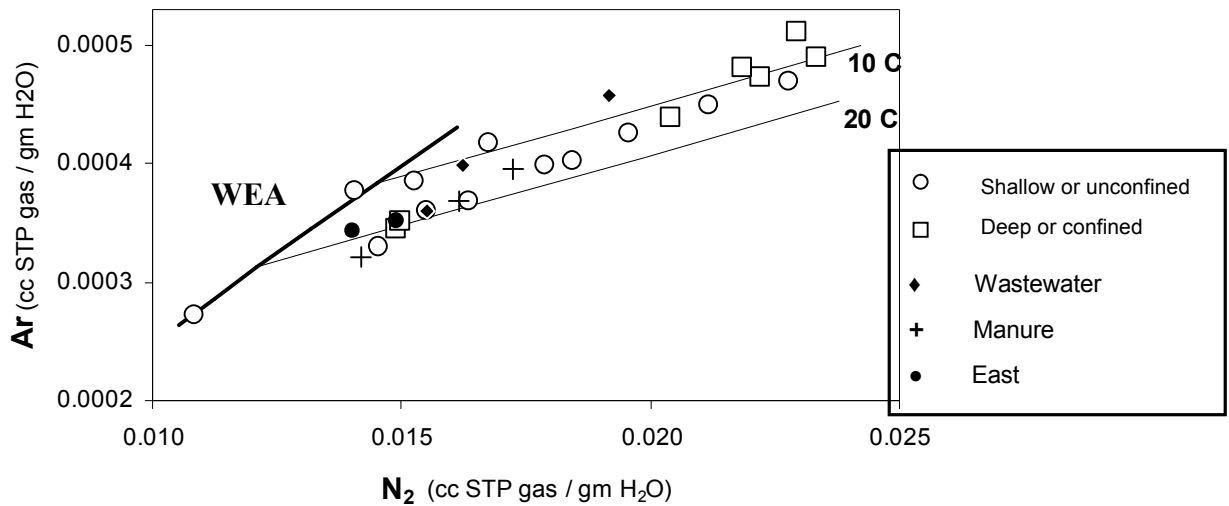


Figure 5. Dissolved nitrogen versus dissolved argon. The WEA (“water equilibrated with air”) line represents the nitrogen and argon ratio expected based on equilibrium solubilities of the gases. The excess air lines are projected by assuming that excess air is the result of complete dissolution of entrapped air bubbles. All samples fall, within error, on or above the projected region of ratios for dissolved excess air. Any samples above this region likely experienced partial air bubble dissolution during recharge.

Groundwater Sources

We use stable isotopes of water to establish groundwater provenance. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ 2003 data fit onto a trendline falling slightly below the Global Meteoric Water Line with a slope generally parallel to it, suggestive of a local meteoric water line trend (Figure 6). The nearest station for which long term precipitation data have been collected is in Santa Maria, CA (GNIP, 2004) 400 km to the south. The Livermore data fall within the general range defined by Santa Maria precipitation isotopes, although the Livermore groundwater’s $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are somewhat lighter due to its higher elevation and inland location. Adherence to a Local Meteoric Water Line (LMWL) without significant deviation provides evidence that this groundwater experienced little evaporation prior to recharge.

These isotopic data are also useful in distinguishing between the three most probable sources of water to the aquifer: precipitation, imported South Bay Aqueduct (SBA) water, and ambient groundwater old enough to predate California’s history of large-scale water manipulation. Originating mostly at higher elevations in the Sierra Nevada Mountains, SBA water is isotopically lighter than local precipitation. SBA water recharges the aquifer along Arroyo Mocho from April to November and also makes up 95% of irrigation water and approximately 80% of domestic water in the area (Segura, 2004). Older ambient groundwater, identified by its lack of tritium, appears at the heavier end of the observed trend. The various mixing fractions of the three

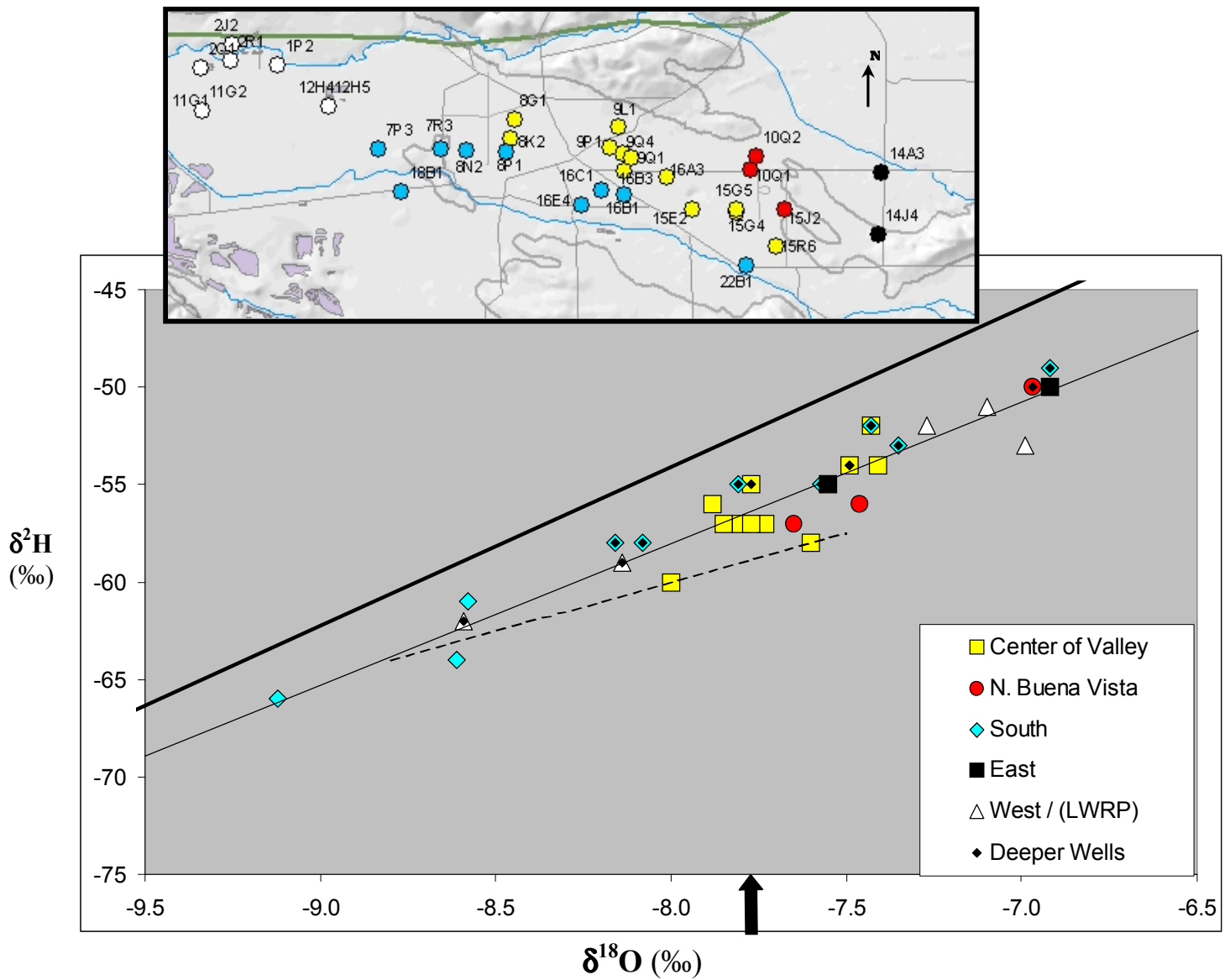


Figure 6. Well water samples fall on a line subparallel to the global meteoric water line in $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ space. The mean $\delta^{18}\text{O}$ value measured in Livermore precipitation is shown by the arrow. Samples in the southern (blue symbol) group have lighter stable isotope values and a significant component of imported South Bay Aqueduct water.

possible sources of water are evident in the isotope data, but the large range observed in local precipitation (-14.8 to -0.3‰ $\delta^{18}\text{O}$ with a mean of -7.75 ; pers. comm., T. Rose) prevents quantitative determination of the three fractions (Figure 6). In general, local precipitation is a dominant source, and the shallow and proximal wells to Arroyo Mocho (i.e. wells 22B1, 16E4) contain higher fractions of SBA water, while deeper wells (i.e. wells 10Q2, 7P3) have high fractions of older groundwater.

The groundwater flow system can be further constrained by defining the recharge area using tritium-helium residence time data, with the youngest ages representing locations of most recent recharge (Figure 7). The shallow wells nearest the arroyo have

residence times of less than one year, and most other shallow wells have residence times of less than ten years. These data suggest diffuse recharge throughout the study area with substantial recharge and relatively rapid groundwater flow along the arroyo. Along the coarse sediments of the alluvial channel, there is a general correlation between mid-screen well depth and groundwater mean residence time. Even the deepest alluvial channel well (well 9Q1), however, has a significantly higher fraction of young water than the tritium-free deep western wells that are protected by a series of clay layers (wells 7P3 and 7R3). The primary sources of modern recharge, SBA water and precipitation, are both very low in nitrate and cannot be directly implicated as nitrate sources (State of California, 2004). As discussed in more detail below, recently recharged water with high nitrate concentration has likely entrained nitrate that has accumulated in the vadose zone.

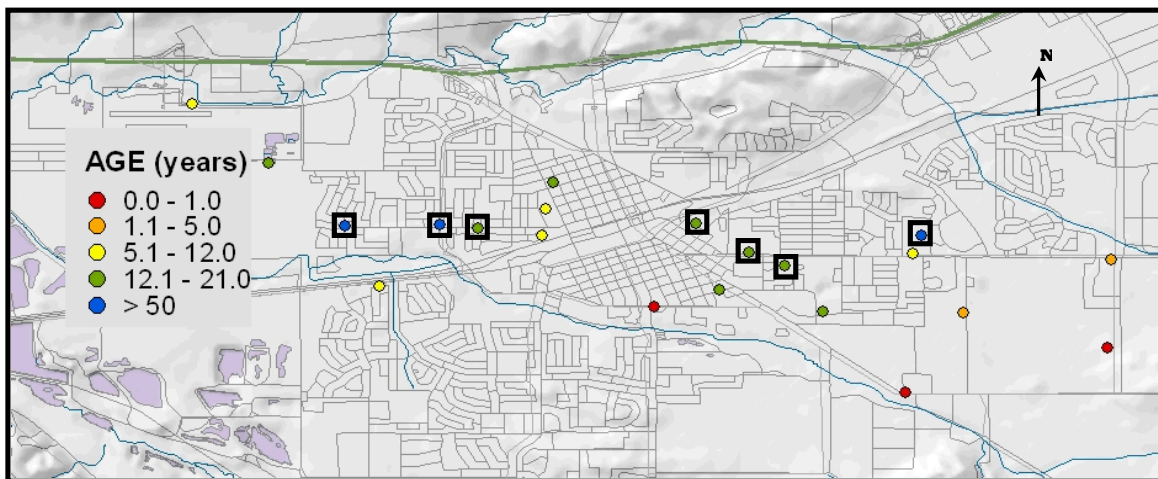


Figure 7. Groundwater ages calculated using the tritium-helium method show very recently recharged water in wells close to the arroyo and on the eastern margin of the basin. Symbols with squares are wells with depths greater than 35m, which in general have older ages.

Groundwater Chemistry

Measurement of additional ion concentrations allows for separation of the nitrate plume into well-defined spatial groups based on differing solute composition. A plot of chloride vs. sulfate shows that data from 71% of the wells lie along a constant ratio trend, indicating the similarity of water type and ion source in these wells (Figure 8). This main trend includes the wells along the alluvial channel flowpath and south to Arroyo Mocho. In the southeast, a relatively high chloride to sulfate ratio separates wells 10Q1 and 15J2 from the rest of the wells in that region, which follow the main trend. Ion data from wells around the LWRP wastewater application area form a distinct lower slope trend, establishing that these wells are dominated by a different water source than the rest of the study area. The low ion end-member of this LWRP trend is defined by the area's deeper, confined wells. These wells have a chloride to sulfate ratio matching that of the main trend, suggesting that the water source impacting the shallow wells does not reach the lower aquifers. Eastern well 14J4, drilled into bedrock rather than alluvium, does not fit into any of the established trends. Wells 14J4 and 14A3 lie in a separate subbasin with different hydrogeological conditions and do not follow data trends observed in the rest of

the valley. For completeness, data were collected and are presented for these wells, but they will not be discussed further.

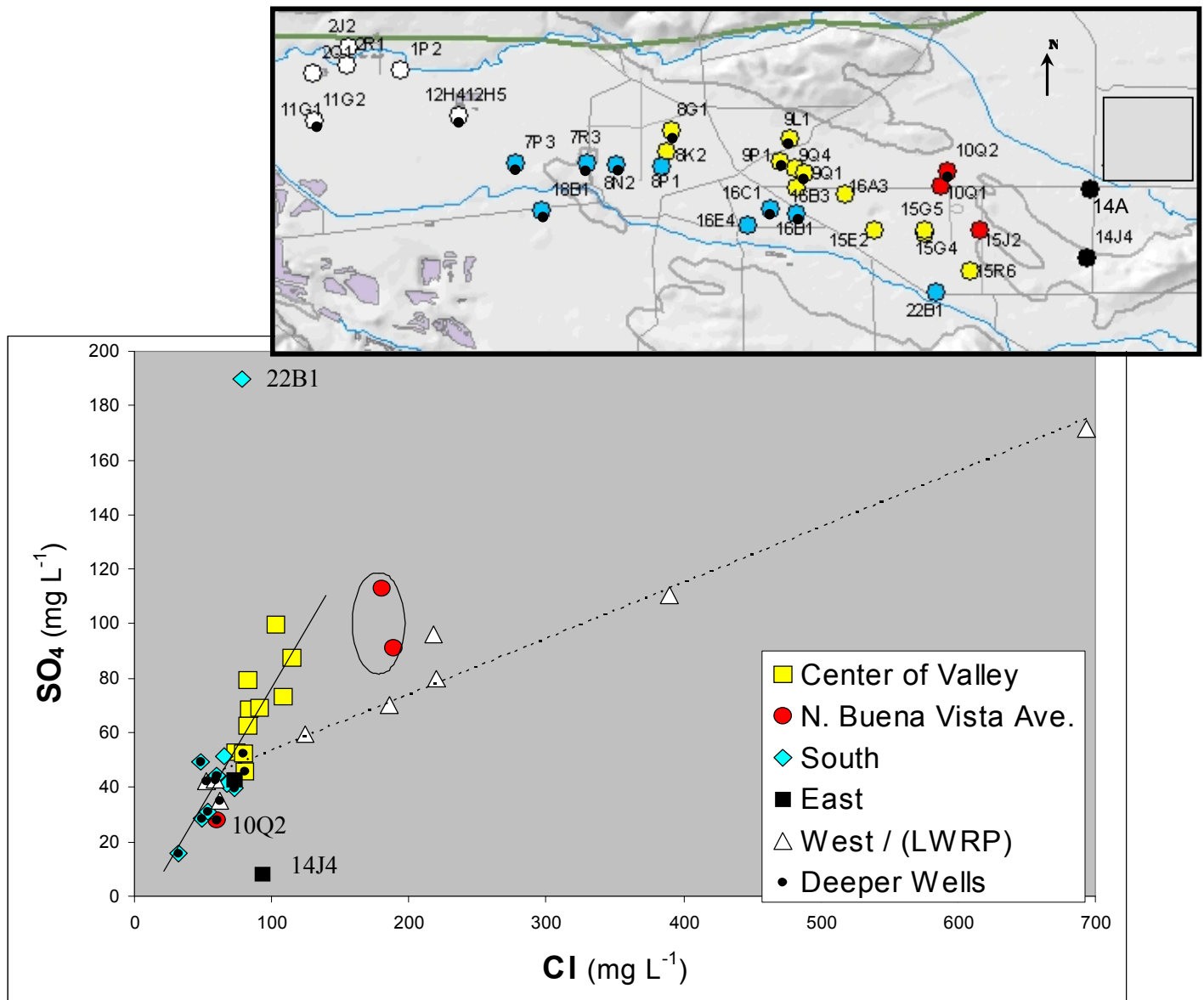


Figure 8. Chloride vs. sulfate compositions. Three spatially distinct water types have been distinguished. Wells within the oval (15J2 and 10Q1) are discussed under the manure source discussion section.

Nitrate Sources

Applied Wastewater

The three distinct groups defined by major ion data as well as by spatial distribution will be further considered individually. In the northwest region around the LWRP, nitrate isotope data confirm that the shallow wells here have a different nitrate source than in the rest of the study area (Figure 9). Shallow nitrate- $\delta^{15}\text{N}$ values are between 13.0‰ and 29.2‰, in the range expected for treated wastewater effluent (Jordan *et al.*, 1997; Griggs *et al.*, 2003), and nitrate- $\delta^{18}\text{O}$ values are the highest of all measured samples, consistent with the effects of wastewater processing (Figure 9b). These data signify that irrigation with reclaimed wastewater is the source of this area's distinctive geochemical signature. Water in the deeper wells, unimpacted by irrigation, has nitrate- $\delta^{15}\text{N}$ values (6.7‰ to 8.8‰) comparable to the other wells that define the main trend in Figure 9b. Stable isotopes of water provide further evidence that the confining layers have prevented applied wastewater from reaching the deeper aquifers; water from these aquifers has an isotopic signature suggesting a precipitation source, while samples from the unconfined layer have heavier $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, likely the result of fractionation during wastewater processing.

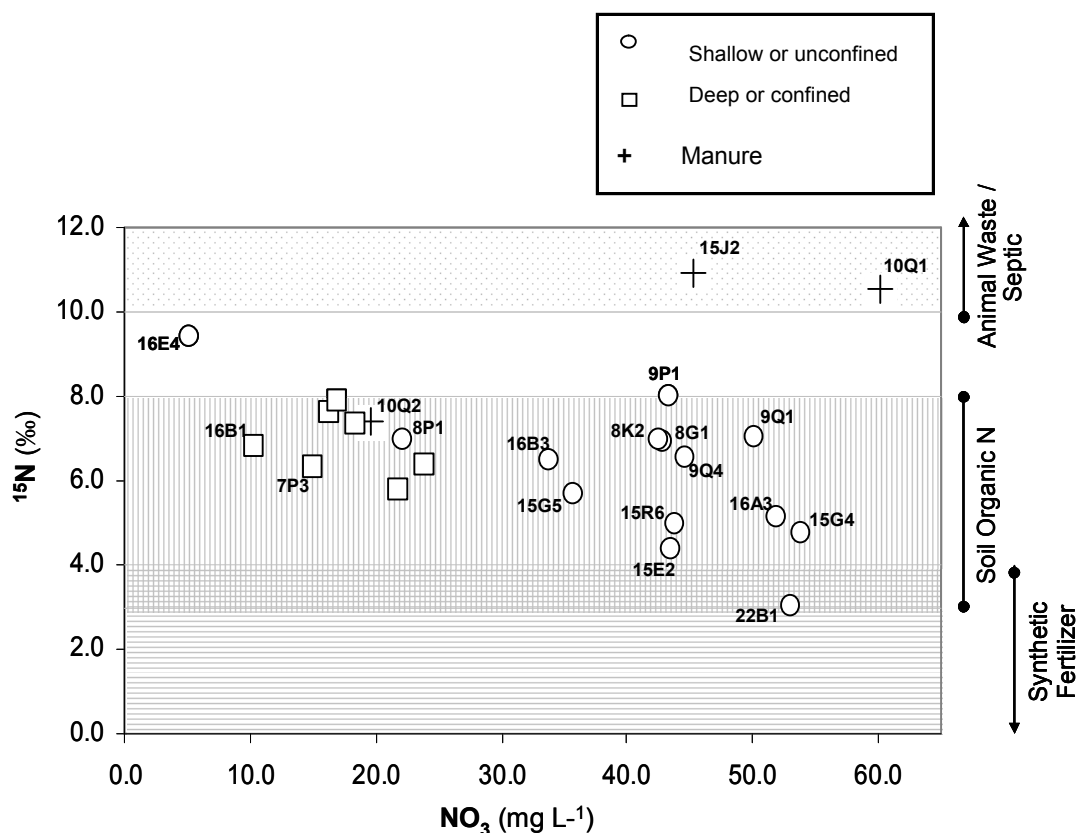


Figure 9a. Nitrate concentrations and $\delta^{15}\text{N}$ values in groundwater. Expected $\delta^{15}\text{N}$ ranges for various sources identified.

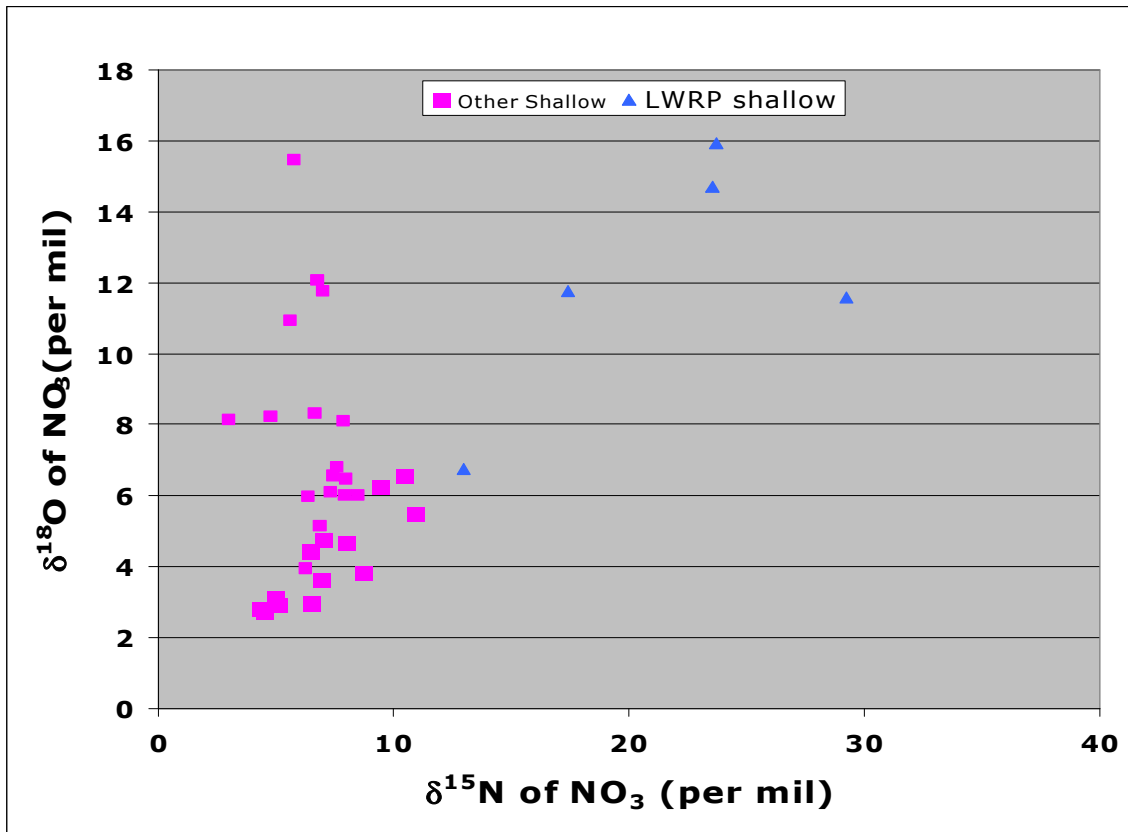


Figure 9b. Shallow wells whose recharge source is treated wastewater from LWRP have isotopic signatures of nitrate that are distinct from other wells and indicate isotopic fractionation by denitrification.

Although this LWRP region was identified as a high nitrate source area in the past (Sylvester, 1983), most of the wells currently have nitrate concentrations well below the MCL (Table 1). The one well within the area of wastewater application for which long term historical data are available, well 2R1, shows concentrations as high as 75 mg L^{-1} in the late 1970s. After modernization of treatment facilities in 1981, nitrate levels began to drop, reaching concentrations around 10 mg L^{-1} in the space of just five years. This demonstrates that the new wastewater treatment methods have been successful at reducing nitrogen loading to the aquifer from reclaimed water irrigation.

Manure

The southeastern region has been identified as the starting point of the high concentration plume. Although the potential nitrate exposures are the same for all of the wells in this area, the ionic composition of wells 15J2 and 10Q1 stands out from the rest (oval area Figure 8). The more northerly flowpath on which these wells lie is likely impacted by a different primary nitrate source than the rest of the valley (Figure 8 and Figure 9a). Measured nitrate- $\delta^{15}\text{N}$ values greater than 10‰ identify animal waste as the nitrate source in these wells, but these isotope data do not distinguish between manure and septic inputs. Examining observed historical trends provides further insight. Time

series reconstructions of past nitrate concentrations at these wells show that both have had a trend of significantly decreasing nitrate concentrations for at least twenty years (Figure 10a). Current nitrate concentrations at both wells are less than a third of peak values and are nearly at the MCL. Although some modern nitrate sources may remain, it seems that a major source has been discontinued or significantly diminished. Because septic and fertilizer input in this area have remained steady or have increased over the last few decades, historical livestock waste (most active inputs approximately 1950 to 1975) is implicated as a major contributor to nitrate contamination along this flowpath.

Tritium-helium mean residence times of 4 and 9 years in wells 10Q1 and 15J2 demonstrate rapid recharge in this manure-impacted area. As discussed above, however, the contamination in this water comes from sources that were present at the land surface decades ago. This describes a situation in which historical contamination stored in the vadose zone is being flushed into the groundwater over time. This rapid flow and historically-sourced nitrate contamination affects only the shallow part of the aquifer; well 10Q2, 80 m deeper than well 10Q1, has a nitrate concentration of 19.6 mg L^{-1} , compared to 60.2 mg L^{-1} in the shallow well. No tritium was detected in well 10Q2, indicating that water at this depth is at least 50 years old. The sum of the evidence therefore suggests limited vertical flow and little interaction between the upper and lower aquifers in this area of thin alluvial fill.

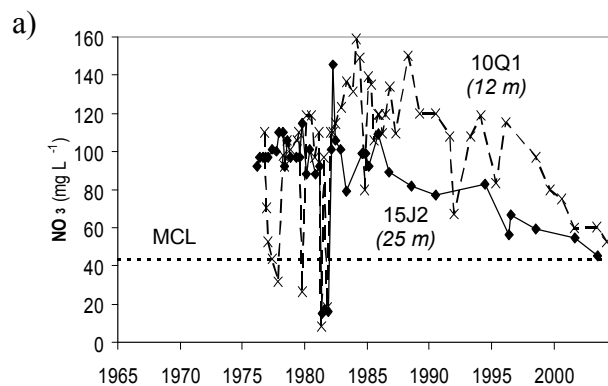
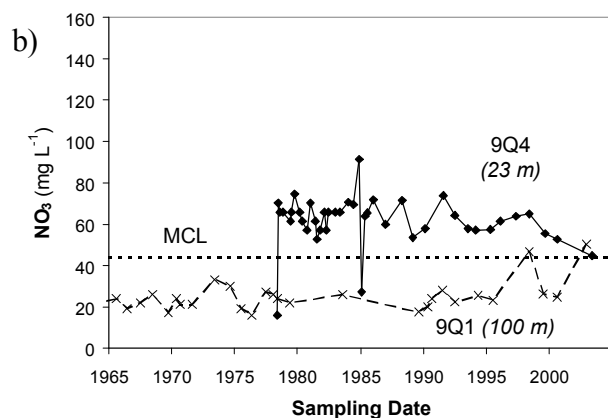
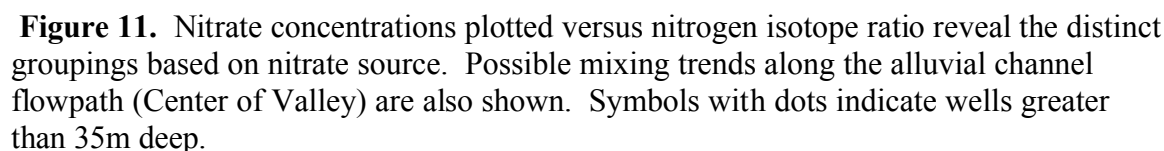


Figure 10. Nitrate concentration time series data. Drinking water maximum contaminant level (MCL) shown for reference. Well depths indicated. **(a)** Manure flowpath. **(b)** Alluvial channel flowpath.



Fertilizer and Soil Organic Nitrogen

To supplement nitrate-source information provided by nitrate concentration and isotope data, historical ion data combined with residence time measurements yield critical information regarding the impacts of natural background processes versus the impacts of past or present anthropogenic processes. It is constructive to consider data grouped by the depth of the wells and the hydrogeological layers they tap rather than by geographic location alone. The main trend identified by the anion data, which covers a wide area where diffuse recharge and discharge (pumping) complicate the flow system, is considered as two groups. In one group, wells either pump from aquifers confined beneath several aquicludes or else are predominantly screened at depths greater than 80 m. Three deep wells with tritium concentrations of less than 1 pCi/L (wells 7P3, 7R3, and 10Q2; Table 1) provide an archive of groundwater that recharged before major inputs of non-natural nitrate. At these wells, groundwater is not impacted significantly by the shallow zone contamination, suggesting that the nitrate detected here represents a natural background. Yet nitrate concentrations in these wells are between 15 mg L⁻¹ and 20 mg L⁻¹, which is higher than generally expected for nitrate from non-anthropogenic sources (Nolan, 2002). As discussed above, this result can be explained by nitrogen-fixing vegetation in Livermore's semi-arid climate. Nitrate- $\delta^{15}\text{N}$ values between 6.3‰ and 7.6‰ support the hypothesis of soil organic nitrogen as a natural nitrate source. Other deep wells produce groundwater that is a mixture of post-modern tritiated water and water recharged more than 50 years ago. The higher nitrate values observed at these wells reflect young, high nitrate water mixed with 'old' groundwater, which likely dilutes the nitrate concentration to some extent. Deeper penetration of younger water in these wells is the result of the influence of pumping patterns and of location with respect to the arroyo and to overlying alluvial fill.



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nitrate levels have been increasing slowly, so that even the deepest well (9Q1) has recently surpassed the MCL (Figure 10b). This supports the depiction of a separate nitrate source along this flowpath and suggests a source with continuing input rather than a historical source. Furthermore, groundwater pumping for municipal supply from wells screened over long intervals may draw nitrate contaminated water to greater depths in the discharge area.

Well 22B1 is particularly useful in providing the chemical and isotopic signature of the contaminated alluvial channel end-member, since it is situated at the head of the source area, has a high nitrate concentration, and produces very recently recharged groundwater. This well is at the southeastern perimeter of the nitrate contamination plume and adjacent to Arroyo Mocho (Figure 11). Multi-tracer data reveal unusual conditions in this area that provide important insight into the origin of the contamination. Well 16E4 is another shallow well adjacent to the arroyo but several kilometers to the west of well 22B1. Light stable isotopes of water at both wells indicate that they draw the majority of their water from recharge of SBA water along the arroyo (Figure 6). Tritium-helium residence times of less than one year at both wells also indicate that rapid recharge from the arroyo is a significant source of shallow groundwater proximal to the arroyo (Figure 7). Despite this evidence that these two wells have the same source of water, their observed nitrate concentrations are very different. Well 16E4 generally has less than $10 \text{ mg L}^{-1} \text{ NO}_3$ while well 22B1 historically fluctuates between 30 mg L^{-1} and $80 \text{ mg L}^{-1} \text{ NO}_3$ (unpublished data, Zone 7, 2003). SBA water contributes little nitrate, with an average concentration over the last 10 years of 2.5 mg L^{-1} (State of California, 2004). To reach the high nitrate levels seen at 22B1, then, recharge through the arroyo must mobilize a local source of nitrate in its short travel time to the well. This represents a substantial amount of nitrogen moving through the system, and must either be supplied by a large reserve stored in the soil or vadose zone or by a source that is continually being replenished. Either a soil or fertilizer source, therefore, is implicated as the source of nitrate in this location.

All nitrate concentrations measured in the alluvial region were greater than 33 mg L^{-1} and $\delta^{15}\text{N}$ values were less than 8‰ (Figure 11). Well 22B1 and well 15G4 have the highest nitrate concentrations, at 53.1 and 53.8 mg L^{-1} . The nitrate- $\delta^{15}\text{N}$ values here are in the low range expected for synthetic fertilizer (3.1‰ and 4.8‰, respectively). This overlaps the low end of the range for nitrate from reduced soil nitrogen, another potential source given these wells' location downgradient of vineyards and grassland. Although nitrogen isotopes alone cannot distinguish between these two sources, it is unlikely that concentrations as high as 80 mg L^{-1} , which have been measured at well 22B1, result from soil nitrogen inputs alone. As groundwater flows from the southeast to the northwest along the alluvial channel flowpath, the trend, originating at well 22B1, is towards decreasing nitrate concentrations and increasing $\delta^{15}\text{N}$ values (Figure 11). In the absence of denitrification, remineralizing nitrate in the soil and mixing with uncontaminated water would result in such a trend toward decreased nitrate concentrations and increasing nitrate- $\delta^{15}\text{N}$ values into the range expected for soil nitrogen (Choi, 2003).

Nitrate- $\delta^{18}\text{O}$ data provide further evidence for a fertilizer source of nitrate in this area. Wells 22B1, 15G4, and 15G5 have nitrate- $\delta^{18}\text{O}$ values between 8.1‰ and 10.9‰ (Table 1), relatively high compared to the values found at the other shallow wells with low $\delta^{15}\text{N}$, which range from 2.8‰ to 4.8‰ nitrate- $\delta^{18}\text{O}$. High nitrate- $\delta^{18}\text{O}$ is consistent

with a synthetic fertilizer nitrate source. Nitrate from synthetic fertilizer generally has a nitrate- $\delta^{18}\text{O}$ value around 23‰ (Kendall and Aravena, 2000), while ammonium nitrate fertilizer, with approximately 50% of its oxygen from fertilizer nitrate and 50% from nitrified fertilizer ammonium, would be expected to have a nitrate- $\delta^{18}\text{O}$ value of approximately 13‰ in this environment (Aravena *et al.*, 1993).

According to our interpretation of the available data, which include nitrate distributions and isotopes, water compositions, stable isotopes of water, and tritium-helium residence times, several flowpaths originate in the southeastern region of the valley, one primarily impacted by historical manure sources and the other with a significant modern synthetic fertilizer component. Inverse geochemical modeling validates that this is a realistic explanation by postulating mixing ratios and sets of mass transfer reactions to explain differences in chemical composition between water samples along these flowpaths. Selected inverse modeling results for both flowpaths (i.e., mass transfer reactions that plausibly explain differences in major ion water chemistry between nitrate-impacted and background water compositions) are compared in Figure 12. These modeling results suggest that the loading of an organic carbon component (and its subsequent oxidation) can be associated with the manure flowpath but is not required for the alluvial channel flowpath. The inverse modeling also suggests a significant role for dilution along the manure flowpath – most probably from local rainfall recharge. As stated previously, however, variability in the oxygen isotopic composition of the local precipitation precludes direct validation of this model result. Inverse geochemical models are typically non-unique, and the set of results shown in Figure 12 is only one example of the multiple variations that are possible to account for observed behavior. Other postulated reactions along both flowpaths include replacement of Mg-rich carbonate phases with generally more Ca-rich equivalents as well as addition of salts and/or ion exchange reactions. Nevertheless, a valid inverse model that is consistent with the water composition evolution hypothesis formulated upon separate lines of evidence, described above, is of significant utility in validating the internal consistency of this hypothesis.

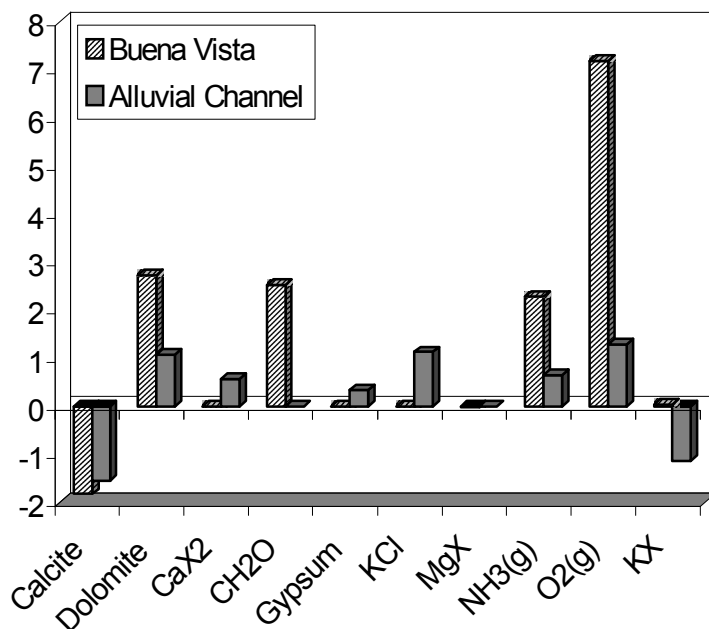


Figure 12. Geochemical modeling results. One set of inverse modeling results indicating mass transfer reactions that can account for differences in nitrate-impacted and background water compositions along the manure and alluvial channel groundwater flowpaths. In addition to the mass transfer reactions plotted, the manure flowpath includes a 43% dilution of the nitrate-impacted water with rainwater. This scenario requires input of organic carbon along the manure flowpath, but not along the alluvial channel flowpath.

Conclusions and Recommendations:

In this study, the separation of nitrate sources introduced decades ago is made possible by a multiple-analysis approach using current and historical data. Stable isotopes provide information about water sources, while tritium-helium age dating defines groundwater residence times and transport behavior. In addition, dissolved gas and nitrate isotope evidence indicate that nitrate moves conservatively in the groundwater, which simplifies source attribution. Nitrate isotope measurements are then combined with information about land use history to identify contaminant sources. This integrated approach reveals a much larger role for fertilizer and natural soil nitrogen than suggested by prior assessments, which used source mass and plume delineation methods to attribute most of the contamination to septic tanks and livestock. In addition to identifying contaminant sources, these methods offer a deeper understanding of how the severity and extent of contamination is affected by hydrogeology and groundwater management practices. In this case, the nitrate problem is amplified by artificial recharge in the source area, a region where the aquifer is vulnerable because it is unconfined and experiences high vertical recharge. This approach can be widely applied to other regions with historical nitrate inputs and can provide valuable information to water managers in evaluating future mitigation strategies.

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Well ID	Well Type ^b	Well Screen		NO ₃ ^d mg/L	$\delta^2\text{H}^{\text{d}}$ (H ₂ O)	$\delta^{18}\text{O}^{\text{d}}$ (H ₂ O)	$^3\text{H}^{\text{d}}$ age	Recharge Temp ° C	$\delta^{15}\text{N}^{\text{d}}$ (NO ₃)	$\delta^{18}\text{O}^{\text{d}}$ (NO ₃)
		Top <i>m below surface</i>	Bottom		----- <i>per mil</i> -----				----- <i>per mil</i> -----	
1P2	MW	12.2	13.7	8.4	-53	-7.0	8	14.4	23.6	15.9
1P2	MW	same as above		8.2	-52 ^e	-6.9	-	-	23.6	14.7
2J2	MW	9.5	12.5	8.8	-51	-7.1	-	-	29.2	11.6
2Q1	MW	10.7	13.7	23.3	-52	-7.3	-	-	17.4	11.8
2R1	MW	6.4	7.9	16.6	-53 ^f	-7.3	-	-	13.0	6.7
7P3	PS	131.1	149.3 ^c	15.0	-49	-6.9	>50	11.8	6.3	4.0
7R3	PS	125.0	161.0	16.3	-53	-7.4	>50	15.1	7.6	6.8
8G1	PS	36.6	138.7	42.8	-55	-7.8	21	15.7	6.9	5.2
8K2	MW	19.5	21.0	42.5	-56	-7.9	10	19.8	7.0	3.6
8N2	PS	42.7	157.0	17.0	-58	-8.1	14	15.8	7.9	8.1
8P1	PS	37.2	80.2	22.1	-61	-8.6	9	15.5	7.0	4.8
9P1	PS	58.5	150.0	43.3	-52	-7.4	21	15.8	8.0	6.5
9Q1 ^a	PS	85.4	100.6 ^c	50.1	-54	-7.5	16	15.5	7.8	11.8
9Q4	MW	21.3	22.9	44.7	-57	-7.8	10	17.2	6.5	4.4
10Q1	MW	10.4	11.9	60.2	-56	-7.5	9	-	10.5	6.6
10Q2	MW	90.9	99.1	19.6	-50	-7.0	>50	-	7.4	6.6
11G1	MW	30.5	33.5	50.4	-53 ^f	-6.7	-	-	8.7	3.8
11G2	MW	70.1	103.7	12.0	-66 ^f	-8.8	-	-	8.5	6.0
12H4	MW	56.4	79.3	13.6	-62	-8.6	7	13.1	7.9	6.0
12H5	MW	109.8	118.9	15.0	-59	-8.1	12	-	6.7	8.3
14A3	MW	30.5	32.0	25.0	-55	-7.6	5	16.9	8.1	4.7
14J4	PV	30.5	71.6	19.5	-50	-6.9	<1	18.5	4.5	2.8
15E2	PV	31.7	57.6	43.5	-57	-7.7	16	19.7	4.4	2.8
15G4 ^a	PV	unk.; < 33.5		53.8	-60	-8.0	-	-	4.8	8.2
15G5 ^a	PV	12.2	30.5	35.7	-54	-7.4	-	-	5.7	10.9
15J2	PV	33.8	40.8 ^c	45.3	-57	-7.6	4	17.6	10.9	5.5
15R6	MW	unk.; < 17.7		43.8	-58	-7.6	-	-	5.0	3.1
16A3	MW	44.2	73.2 ^c	51.8	-57	-7.8	16	21.6	5.2	2.9
16B1 ^a	PS	42.7	118.9	10.3	-55	-7.8	18	-	6.8	12.1
16B1	PS	same as above		21.8	-58	-8.2	-	13.0	5.8	15.5
16B3	PV	0.0	24.4	33.8	-57	-7.9	-	20.4	6.5	3.0
16C1	PS	87.8	159.5	18.4	-55	-7.6	-	13.3	7.4	6.1
16E4	MW	10.7	12.2	5.2	-66	-9.1	<1	11.8	9.4	6.3
18B1	PS	57.9	141.8	23.9	-52	-7.4	11	14.5	6.3	6.0
22B1 ^a	MW	13.7	15.2	53.1	-64	-8.6	<1	-	3.1	8.1

^a Collected in 1/03. All other samples collected between 6/03 and 8/03. Multiple samplings at 1P2, in 6/03 and 8/03, and at 16B1, in 1/03 and 7/03.

^b MW = monitoring well; PS = public supply well; PV = private well.

^c Longest of multiple screens. Also screened at: 7P3 – 91.5 to 97.6 m; 9Q1 – 3 8 m screens from 103.0 to 140.5; 15J2 – 23.2 to 24.7 m; 16A3 – 27.7 to 36.9 m.

^d Average Errors: NO₃ (±2.7%), Cl (±4.6%), SO₄ (±1.7%), $\delta^2\text{H}$ H₂O (±0.9‰), $\delta^{18}\text{O}$ H₂O (±0.1‰), ³H (±2 yr), $\delta^{15}\text{N}$ NO₃ (±0.3‰), $\delta^{18}\text{O}$ NO₃ (±0.9‰), N₂ (±2% standard deviation [s.d.]), Ar (±2% s.d.).

^e Data provided by Zone 7. ^f Measured at LLNL.

Table 1. Well data and chemical and isotopic analyses of samples.

Science & Technology REVIEW

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National Nuclear
Security Administration's
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Innovative Technologies to Protect Water Supplies

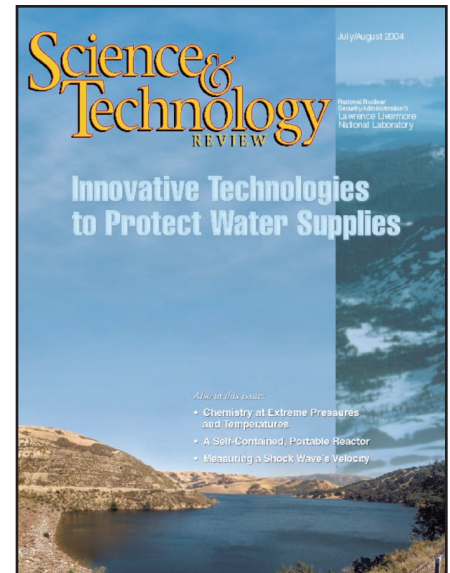
Also in this issue:

- Chemistry at Extreme Pressures and Temperatures
- A Self-Contained, Portable Reactor
- Measuring a Shock Wave's Velocity



About the Cover

Ensuring plentiful water supplies is becoming a critical issue in California. The state's underground aquifers are being consumed at an increasing rate, and contaminants and climate patterns may affect the adequacy of supplies. As described in the article beginning on p. 4, a team of Laboratory scientists is pursuing a three-year initiative to address these challenges by developing tools to evaluate the state's water-supply infrastructure, protection and purification efforts, and flood control. The cover shows two components of California's intricate system. The Del Valle Reservoir near Livermore is one of many reservoirs used to store water. Melting snow from the Sierra Nevada feeds the state's reservoirs and rivers during the spring and summer.



Cover design: Dan Moore. Reservoir photo: Michael Anthony

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Features

3 Technologies to Address California's Water-Supply Challenge

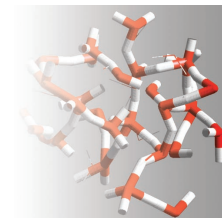
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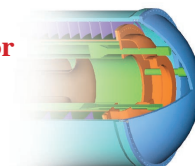
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Technologies to Address California's Water-Supply Challenge

THE growth of California's economy in the 20th century depended on large investments in the state's infrastructure, including major water-supply projects implemented by local, state, and federal agencies. In the 21st century, the state must continue to address important challenges to ensure that it has the water resources needed to sustain continued economic and population growth.

The 1987–1992 drought prompted aggressive moves by urban water agencies to improve water conservation efforts. After the drought, continued conservation provided much of the water for urban growth during the past decade. With California's population increasing at about 500,000 people per year, the state will need new supplies and storage facilities to maintain the reliability of its water supply—particularly during drought conditions.

Where will California find this “new” water? Part of the supply will undoubtedly come from even better water conservation programs, and agricultural water districts may transfer supplies to urban agencies. Other options include building new dams and conveyance facilities or expanding old ones, reusing wastewater, and desalinating seawater. The state may also decide to increase its reliance on groundwater to meet dry-year demands. Any combination of these options will present environmental consequences that must be addressed.

No matter which choices are made, water agencies will have a more difficult time balancing the increasing demands for water with the available supplies because the state's primary source of freshwater—snowmelt from the Sierra Nevada—may be at risk. Each summer, as the Sierra snowpack gradually melts, the water is stored for distribution throughout California. But hydrologic trend analyses and climate simulations now indicate that this runoff may occur earlier in the spring. Many of the state's reservoirs cannot accumulate supplies from an early spring runoff because flood-control regulations limit the amount of water they can store at this time of year. The unfortunate result of this small change in timing is that the overall annual yields from reservoirs may decrease because excess water must be released to avoid flooding.

To make up for the reduced yield of surface reservoirs, California must increase its use of groundwater reservoirs. Although the state has major aquifer systems, many are contaminated with industrial and agricultural chemicals. For example, nitrate from domestic and agricultural sources has contaminated thousands of the state's drinking water wells. Other

contaminants also threaten groundwater supplies, including the gasoline additive methyl tertiary butyl ether, or MTBE, and perchlorate, an oxidizing agent.

Given these problems, California water agencies may need to consider nontraditional sources: urban wastewaters, impaired groundwater, and seawater. However, with current technologies, the cost to treat these sources will be about two times more than it is for existing water supplies, and competing demands for the required energy will substantially add to the overall cost. Clearly, California's success in the 21st century depends on developing solutions to these emerging challenges. But unlike past water-supply projects, which relied primarily on engineering expertise for implementation, future solutions will depend on advanced science and technology.

Lawrence Livermore has a significant opportunity to contribute its expertise to this area, as described in the article beginning on p. 4. For example, the Laboratory's advanced climate and hydrologic simulations can be used to predict future climate patterns and how changes to climate may affect water supplies. Until recently, water managers have had only the historic data to help them plan new infrastructure projects, which will operate far into this century. Applying Livermore's ability to measure, characterize, and simulate the complex biogeochemical processes that control groundwater contamination will benefit managers who increasingly rely on groundwater sources. The development of energy-efficient selective separation technologies tailored to remove specific contaminants would constitute a major advance in water treatment. Collectively, these applications will give water agencies the tools they need to meet the increasingly difficult challenges that lie ahead.

■ C. K. Chou, associate director of Energy and Environment, retired in June 2004.

Helping Water Managers Ensure Clean

Livermore experts are developing advanced models and new methods to help protect California's

MOST Americans take cheap and plentiful supplies of pure drinking water for granted. Some even consider it to be an inalienable right. However, clean water sources, especially pristine underground aquifers, are being consumed at an increasing rate, and contaminants and changing patterns in rain and snowfall are threatening the adequacy of supplies.

Ensuring plentiful water supplies is becoming a critical issue in California,

which uses 10 percent of the nation's freshwater. State water managers are closing many contaminated or impaired drinking wells; Sierra snowpacks have diminished in recent years; and the state's farmers, fishermen, environmentalists, and city dwellers cannot always agree on the best uses for a limited supply.

California is not alone with respect to these issues. They are relevant throughout the western U.S. and are becoming more so in other parts of the country. They also are critically important in highly populated and developing nations such as China, India, and Mexico as well as in many parts of Africa and the Middle East.

and Reliable Supplies

precious water sources.

To consider possible methods to address these challenges, a team of Lawrence Livermore scientists is working on a three-year Water Initiative that is managed by Livermore's Energy and Environment (E&E) Directorate. The initiative, now in its second year, marshals Livermore's expertise in chemistry, materials science, environmental science, microbiology, and computer modeling. The team's goal is to develop innovative tools that water resource managers can use to make informed decisions about the state's water-supply infrastructure, protection and purification efforts, and flood control. In so doing, the scientists are helping to position the Laboratory as a leader in the science and management of water resources.

Three Projects Tap Lab Expertise

"We are creating tools and methods that will serve the water management

community," says Robin Newmark, who leads the E&E Water and Environment Program as well as the Water Initiative. When Newmark and her colleagues studied the problems facing California water managers, they found three areas where Livermore's expertise could make the greatest contributions: providing better predictive models, improving the scientific understanding of water contamination, and developing more cost-effective technologies for purifying water.

The three resulting scientific projects that form the Water Initiative are funded by Livermore's Laboratory Directed Research and Development Program. Additional institutional funding supports planning and outreach activities aimed at establishing relationships with water managers at the local and state level.

The first project links climate and surface hydrology models run on

Livermore's supercomputers to predict how climate variability can affect the supply of freshwater in the coming decades. The second project studies ways to better understand and manage nitrate, the leading contaminant of California groundwater. The third project focuses on treating contaminated water with new, cost-effective membranes for electrodialysis.

The Department of Energy (DOE) might not seem a logical choice to be leading a water effort, but energy and water are inextricably linked. "Energy security depends on water security," says Newmark. The production of energy is the second largest consumer of freshwater in the nation, after agriculture. At the same time, the processes involved in treating and distributing an abundant supply of clean water depend on having low-cost energy readily available. Nationally, about

The Del Valle Reservoir in California.

4 percent of electricity is used to pump, process, and treat water.

The demands for both energy and water are expected to grow substantially in the next 25 years. "As a result," says Newmark, "a strong federal role is needed to provide scientific research, technology development, and analysis capabilities so

the nation can achieve energy and water security and sustainability."

Simulations Guide Decision Makers

In California, the availability of sufficient freshwater to meet agricultural, urban, fishing, recreational, and other needs depends on properly managing a complex

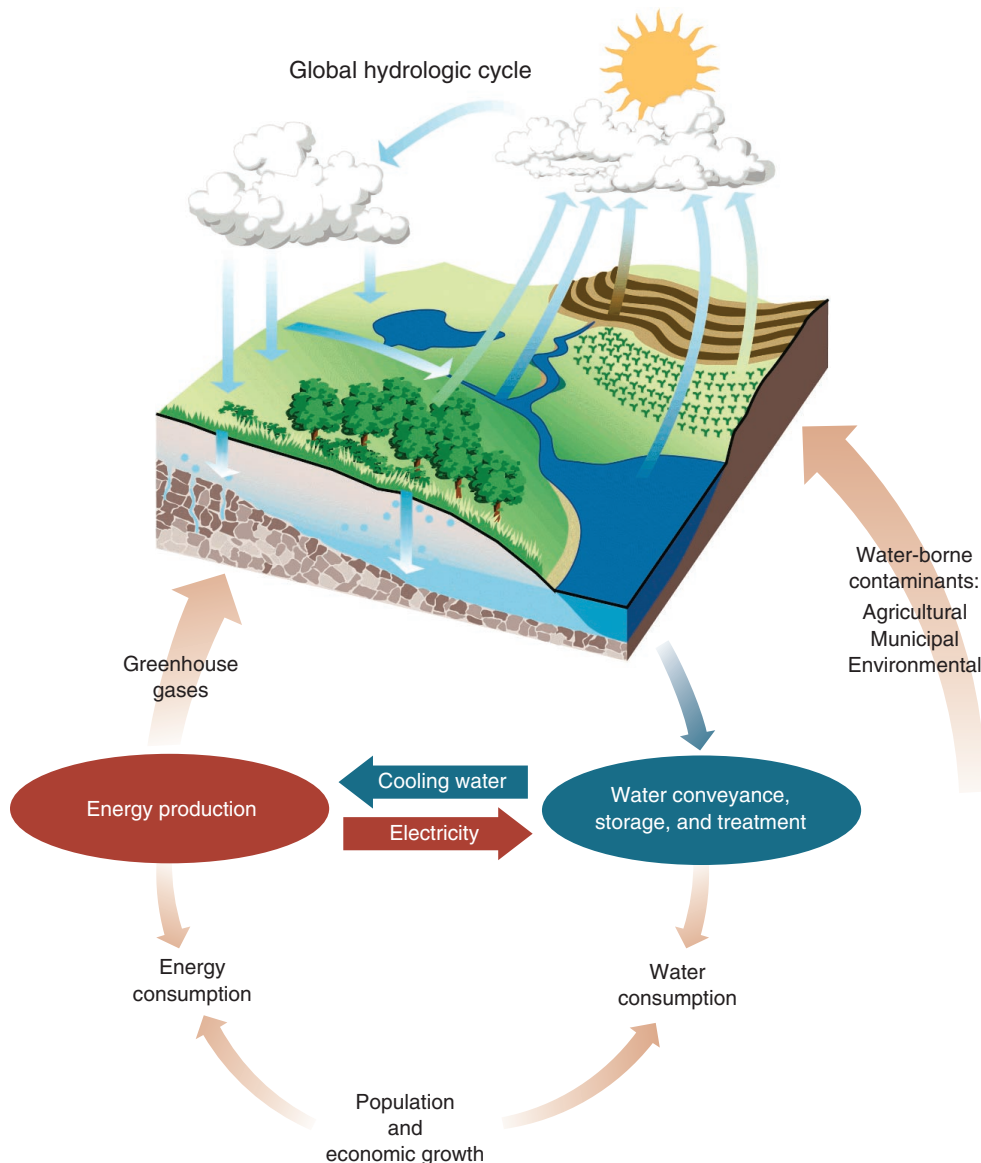
system of water storage and delivery. In making decisions, water managers are guided by past observations of the natural hydrologic cycle, including such factors as rainfall, the water content of snow, and river flow rates.

These observations are useful only if the future behavior of California's hydrologic system is similar to its past behavior. Yet, such an assumption may no longer be correct. If the natural hydrologic cycle continues to change significantly, water management practices must adapt to the new patterns. These changes require building new reservoirs, pipelines, aqueducts, flood-control projects, and treatment plants and in many cases, operating existing facilities differently.

"There's a compelling need for improved water management based on the best models," says Livermore physicist Philip Duffy, who leads the initiative's modeling project and is director of the University of California's (UC's) Institute for Research on Climate Change and Its Societal Impacts. The goal of the modeling effort is to project future changes in the hydrologic cycle in California and determine how those changes will affect the availability of freshwater. Water managers and policy makers would benefit if such projections were available for assessing proposed changes in water management practices.

"We're looking at how water supplies are likely to change during the next several decades," says Duffy. The team's simulations of future water supplies are done on Livermore's massively parallel supercomputers. Fortunately, California's water system is well suited for modeling because most of its supply comes from precipitation or groundwater within the state. Only 5 percent is drawn from out of state (from the Colorado River).

California's water system is dependent on storage of water in reservoirs and in the snowpack. However, few new reservoirs are being built, and increasing



Water and energy are inextricably linked. Energy production is the second largest consumer of the nation's freshwater, after agriculture. The treatment, storage, and distribution of water are dependent on readily available energy. The needs for both resources are expected to grow substantially for the next 25 years.

amounts of precipitation are falling as rain, not as snow.

“The only source that feeds reservoirs and rivers in the summer is melting snowpack,” says Duffy. Measurements show that snowpack water levels are dropping as California’s climate continues to warm. If that decrease continues, it could reduce late spring and summer stream flows into reservoirs. And unless the state increases its reservoir capacity, additional water supplies cannot be stored during the winter even if river flow rates increase because of the changing precipitation pattern. Ironically, to protect against flooding, water managers may need to lower water levels in reservoirs, effectively reducing the total volume of water in storage. As a result, less water would be available in summer to support agriculture, hydropower production, fisheries, and recreation, thus compounding the state’s need for increased storage capacity.

Linking More Detailed Models

To better understand how these changes will affect California’s water supply, Duffy’s team is using a sequence of models, starting with global climate models and ending with surface hydrology models. Each successive model increases the simulation’s spatial resolution, which improves how closely the results agree with observations. “High spatial resolution is even more important for simulating the hydrologic cycle than it is for simulating climate,” says Duffy.

A model with fine resolution can more realistically represent the topographic features of an area and, thus, its surface temperature, which determines whether precipitation is rain or snow. The spatial pattern of precipitation within California is strongly influenced by topographic variations such as coastal hills, inland valleys, and the Sierra Nevada, so surface hydrology models must map topography at a fine resolution to show accurate routes for surface runoff into rivers.

Duffy’s team generates the initial predictions of the sequence using a global climate model run at a spatial resolution of about 75 kilometers. Although this resolution is much finer than typical for global models, it does not provide enough detail for the project. Data from the global climate models are then used to drive two regional climate models, one with a grid size of 9 kilometers and the other with a grid of 36 kilometers. Having results from two models helps the team estimate uncertainties in the model predictions.

Next, the researchers feed surface temperatures and precipitation data from the regional climate model into a surface hydrology model run with a lumped-mode grid—that is, each watershed is treated as one irregularly shaped grid cell. This simulation is designed to predict snow depth, soil moisture, surface runoff, and

most importantly, selected stream and river flow rates. The spatial resolution is fine enough to provide the detailed information needed by water managers who oversee different watersheds.

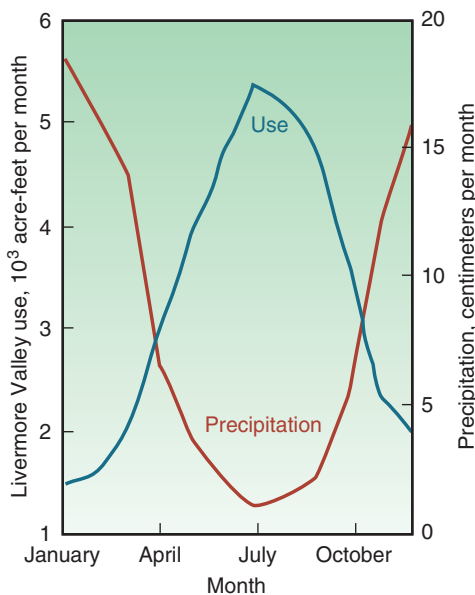
The data generated by the hydrologic model will also be useful for flood control. Because California’s water system is used for both flood control and water storage, water managers need accurate predictions of the maximum values for precipitation, runoff, and river flows as well as the averages over time. That way, they can make informed decisions about how much reservoir capacity is needed to absorb surges in river flow and runoff.

A key component of this project is making the research results useful to water managers and policy makers. “Our approach is to predict exactly the same quantities at the same observation points that water managers use to guide their decisions,” says Duffy. “For example, when we simulate future climate patterns, we’ll predict river flows at locations above major reservoirs. With data from these important reference points, water managers can use the predictions to understand how to operate the water system in an altered climate regime.”

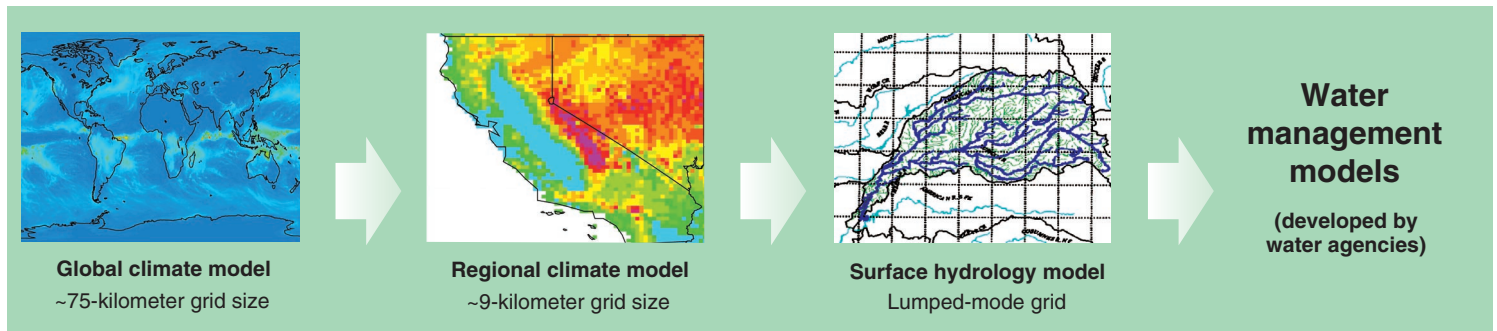
Estimating Uncertainty

Another emphasis of the project is to estimate the uncertainty in the predictions. “We’re emphasizing the uncertainties both from a research perspective and in response to discussions with water managers,” says Duffy. “They gave us a clear message: ‘Tell us the uncertainties associated with your models.’ One approach is to compare results from a range of accepted models.”

The project team has compared the simulations of present and future climates in California provided by 15 global climate models. These models predict surface temperature, precipitation rate, solid moisture content, water-equivalent snow depth, and other meteorological quantities. Because each model was developed at



Melting snowpack is the only water source for California reservoirs and rivers in summer, when water usage increases. For example, as the chart shows, residents of California’s Livermore Valley (blue line) use the most water during summer—the time of lowest precipitation in the Sierra (red line), where much of the valley’s water originates. (1 acre-foot equals 1,214 cubic meters of water.)



Livermore simulations are being used to project future changes in California's hydrologic cycle and determine how these changes will affect the availability of freshwater. Researchers use a sequence of models, and each successive model increases the simulation's spatial resolution. The surface hydrology models are run with a lumped-mode grid—that is, each watershed is treated as one irregularly shaped grid cell.

a different research institution, each one treats climate physics slightly differently. Thus, the models give a range of predictions for both the present and future climates of the western U.S., which provides a measure of uncertainty.

Initial results from this project have led to endorsements by federal, state, and local agencies for a center to address long-term water-supply predictions for California. Such a center would provide projections of regional climate hydrology to water managers, much as the Program for Climate Model Diagnosis and Intercomparison, established at Livermore in 1989, develops methods to validate and compare global climate models. The proposed center would include participants from the major research groups working to improve the science of predicting future water-supply patterns and problems.

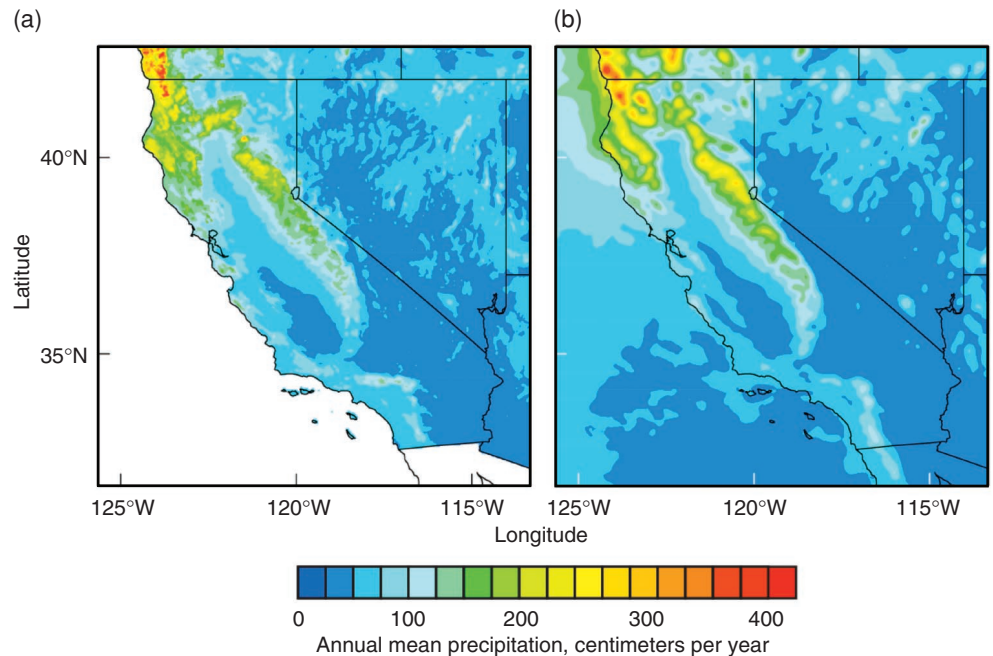
The Threat of Nitrate Contamination

One of the most important tasks for California water managers is to protect the purity of groundwater, which supplies about half of the state's drinking water. However, since 1988, about one-third of the state wells that supply public drinking water have been abandoned, destroyed, or inactivated, frequently because they have been contaminated with nitrate from fertilized farmland, dairies, feedlots, and septic tanks.

Nitrate, a nitrogen–oxygen compound, is a significant source of nitrogen, an essential nutrient. However, high levels of nitrate in drinking water can cause serious illness and sometimes death. Nitrate poses a special risk for infants. It can diminish the oxygen-carrying

capacity of an infant's blood (called blue baby syndrome), which can lead to death. High nitrate levels can also harm the ecosystems of lakes, streams, and the coastal ocean.

Ten percent of active California public supply wells have nitrate contamination



To validate the accuracy of a computer model, scientists compare the model's results with observations. In this example comparison, the Livermore team used (a) the observed mean annual precipitation in the western U.S. from 1971 to 2000 and (b) results from a regional climate model of annual precipitation for that same period. The model's resolution is 9 kilometers.

exceeding the drinking water standard of 45 parts per million, and another 20 percent contain nitrate levels that are significantly above background levels. In agricultural counties, up to 80 percent of groundwater tapped for drinking water is affected or polluted by nitrate. Alternatives such as drilling a new well or treating contaminated water to remove nitrate are costly.

With a better understanding of how nitrate levels in these wells will evolve over time, water managers can decide which approach to use. In addition, their efforts to protect drinking water will be improved if they have more accurate information on how land-use and farming practices affect nitrate levels in groundwater.

The second project of the Water Initiative, which is led by Livermore chemist Brad Esser, is designed to address the nitrate contamination problem. Esser's team is studying the natural processes that control groundwater nitrate movement and degradation. In this effort, the researchers are applying new diagnostic tools and computer models and drawing on Livermore expertise in isotope hydrology, groundwater modeling, and molecular biology. They are studying the problem at the laboratory, farm, and water-basin scales.

Solubility, Stability Are a Problem

Because of its mobility, nitrate readily contaminates groundwater. Nitrate is mobile because it is soluble and stable in oxygen-rich water and does not bind readily to soils. In oxygen-deficient waters, certain bacteria convert nitrate to molecular nitrogen—a harmless component of the atmosphere—in a process called denitrification. Esser and his colleagues are studying microbial denitrification under laboratory and field conditions, so they can determine a groundwater basin's capacity to assimilate nitrate and understand how nitrate distributions will evolve over time.

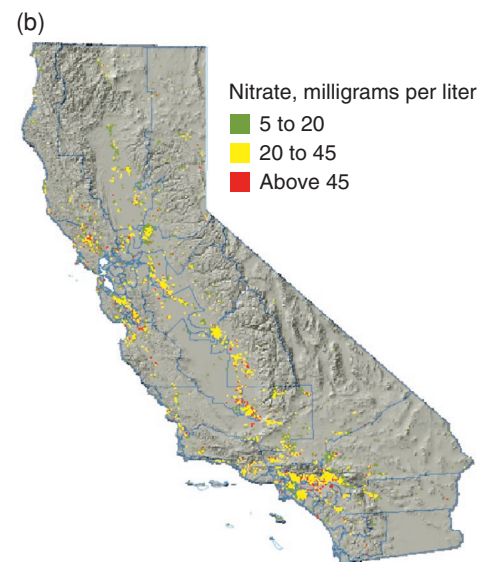
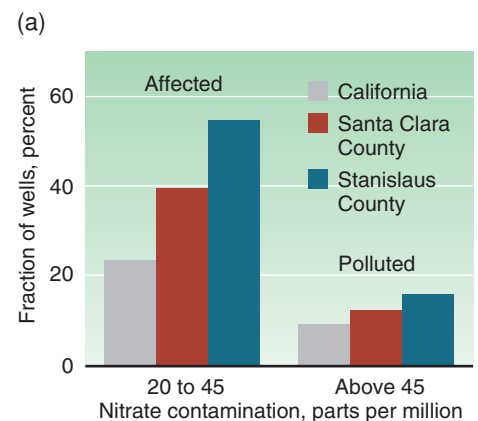
"We are developing better tools to detect and understand denitrification," says Esser. For example, one test is designed to determine whether bacteria capable of denitrification are present and if they are removing groundwater nitrates. The test detects a gene in the bacteria that indicates the presence of enzymes responsible for the process. In addition, Livermore scientists have developed a mass-spectrometry method to quantify the amount of nitrogen that has dissolved in groundwater as a result of denitrification. The two tests allow researchers to study what factors control the rate of denitrification in groundwater.

Water managers also need to know the source or sources of nitrate contamination. For example, if the source is septic discharge, then converting septic tanks to sewer lines will be more effective than implementing a farm fertilizer management program. Esser notes that many water contaminants, such as trichloroethylene, are found in high-concentration plumes with easily identified sources. Groundwater nitrate contamination, however, is often low-level and pervasive, reflecting multiple sources such as septic systems or synthetic fertilizer or manure used on crops, so identifying nitrate sources is more difficult.

To understand groundwater flow paths and trace contaminants such as nitrate back to their source, the Livermore team is combining an isotopic technique to determine groundwater age (see *S&TR*, November 1997, pp. 12–17) with groundwater flow models that take advantage of the Laboratory's supercomputing capability (see *S&TR*, June 2001, pp. 13–21).

For this project, the team is working with colleagues from the UC Cooperative Extension and UC Davis in a study of a dairy farm in California's Central Valley. The scientists are installing multilevel monitoring wells to determine groundwater flow paths and to understand nitrate transport and denitrification.

The team is also working with the Santa Clara Valley Water District to characterize nitrate transport in the Llagas basin, a primary source of the groundwater needed to meet future demands in southern Santa Clara County. The basin has pervasive nitrate contamination in shallow aquifers but little contamination in deep aquifers.



(a) About 10 percent of active California public water-supply wells have nitrate contamination exceeding the drinking water standard of 45 parts per million. In agricultural areas, such as Stanislaus County, up to 80 percent of groundwater is affected or polluted by nitrate. (b) The map shows the extent of nitrate contamination throughout the state.

“Deep wells in the basin do not contain nitrate either because denitrification is occurring or because the deep water is old and uncontaminated,” says Esser. “We’d like to determine which process is at work here. We also want to identify the source of nitrate in the basin’s shallow wells.”

For this project, the Livermore scientists are using geochemical models to identify input of nitrate from synthetic fertilizer and developing analytical methods to distinguish septic discharge from manure as sources of groundwater nitrate. So far, they are finding that shallow wells contain young water, whereas the deeper water is older and oxygen deficient. However, they have found no evidence of denitrification under current conditions, indicating that nitrate contamination has not yet penetrated deeper parts of the basin.

The researchers are incorporating these data into a highly resolved three-dimensional (3D) model of Llagas basin groundwater flow and transport. The flow field is based on a 3D geostatistical model of sediment distribution that is derived from drilling logs of more than 300 wells. Results from these simulations will be used to develop groundwater resources in the basin and protect the basin from future nitrate contamination.

Creating “New” Water

Many wells closed by nitrate contamination could be reopened if a cost-effective treatment were found. One significant cost of the water treatment technologies developed in the 1960s and 1970s is their high energy use. For example, one-half the overall cost of seawater desalination using reverse

osmosis is the cost of energy. Another treatment technology, electrodialysis, is more energy efficient at removing salt from less saline, or brackish, waters. However, even electrodialysis is not a cost-effective treatment method for the growing volumes of marginally impaired waters—those that contain small concentrations of one or more contaminants but are otherwise adequate for domestic use. A better approach would be selective technologies designed to extract only a few problem species, which would reduce both the volume of the waste stream and the overall energy cost for treatment.

The third project of the Water Initiative is focused on providing a cost-effective option for treating these marginally impaired waters. If successful, the new technology would undoubtedly help increase water supplies everywhere. In this project, lead investigators geochemist Bill Bourcier and engineer Kevin O’Brien are creating energy-efficient membranes to replace the solid polymer membranes used in electrodialysis. This approach taps Livermore’s capabilities in computational chemistry and nanomaterials synthesis. Says Bourcier, “We want to use it to treat brackish water in a way that sharply lowers operating costs.”

In electrodialysis, transport of either positively charged ions (cations) or negatively charged ions (anions) through copolymer membranes is driven by a voltage applied by a pair of flat electrodes. The ions are driven toward the electrode with the opposite charge. Water flows between alternate cation-permeable and anion-permeable copolymer membrane sheets sandwiched between the electrodes and separated by spacers. As water flows between the membranes, salt is removed from one compartment and concentrated in adjacent compartments, with up to a hundred or more membrane pairs per stack. A manifold separates the exiting fluid into a relatively salt-free permeate product and a salt-enriched brine for disposal.



Livermore researchers are installing a network of multilevel monitoring wells near a dairy farm in California’s Central Valley so they can study the groundwater flow paths, nitrate transport, and denitrification. The arrow shows the direction of groundwater from an irrigation canal toward the monitoring wells. Manure used on crops is one possible source of nitrate found in groundwater.

The current electrodialysis technology is inefficient because it forces all dissolved ions, including those that are considered benign or healthy, through the solid membranes. The Livermore team is replacing these membranes with “smart” membranes of polycarbonate—the material used to make compact disks—which are then coated with a thin layer of gold. (See the **top left figure** on p. 12.) These smart membranes can be designed to selectively remove only one contaminant of interest by specifying the pore size, voltage, and electric field to attract the target contaminant. For nitrate cleanup, a small fraction of a volt will be applied to each membrane, and the overall electric field will measure 1 to 2 volts per membrane pair.

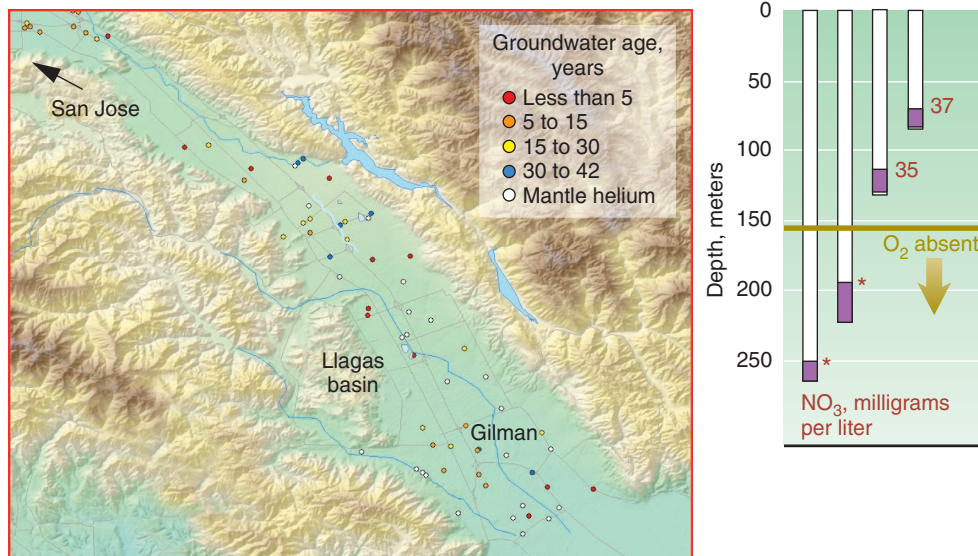
“With current electrodialysis design, every ion is pushed through a solid plastic membrane that has high electrical resistivity and no selectivity,” Bourcier says. “The smart membrane is designed to have low resistivity to ion transport and, therefore, high energy efficiency—up to 50 percent greater than standard electrodialysis.”

Pores Drilled in Smart Membranes

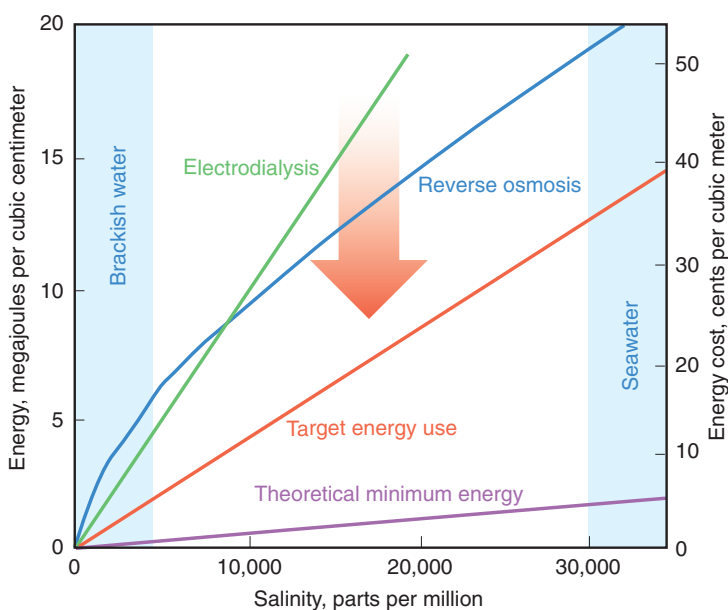
The membranes have pores drilled to an optimal size for selective removal of the ions of interest. If the system is optimized for nitrate ions, for example, those ions will preferentially pass through the pores, while others remain with the stream of water. The nitrates can then be collected in the waste stream.

The pores are created with an etching process using Livermore’s ion-beam technology. For nitrate treatment, the membrane pores are about 10 nanometers in diameter. (See the **bottom left figure** on p. 12.) Current polycarbonate membrane samples contain about 1 billion holes per square centimeter.

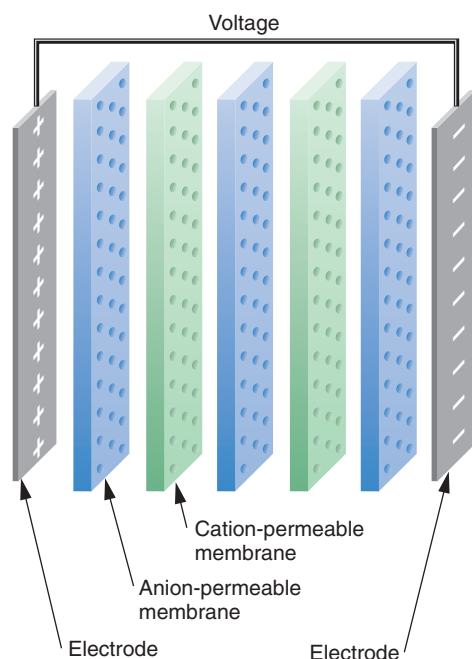
Membranes are being designed using quantum mechanical modeling, which simulates the ions of interest in electrolyte solutions in varying concentrations. The modeling work, which is done on



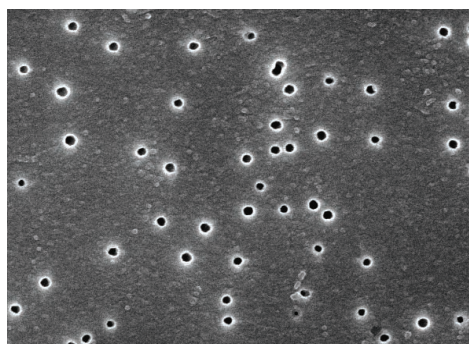
Livermore is characterizing the Llagas groundwater basin, which is managed by the Santa Clara Valley Water District. As shown in data from wells at one location (Gilman), the basin has pervasive nitrate (NO₃) contamination in shallow aquifers but little contamination in deep aquifers, where oxygen (O₂) is absent. (* = less than 1 milligram per liter.)



Livermore researchers are evaluating a modified electrodialysis setup to lower the energy costs for this process by 50 percent. If the goal is met, electrodialysis would become a much more important technology in treating brackish water.



Livermore's modified electrodialysis technology replaces the solid polystyrene membranes with "smart" membranes of gold-coated polycarbonate. By specifying the pore size, voltage, and electric field that will best attract and isolate a target contaminant, researchers can design each membrane to selectively remove only one contaminant of interest.



This image shows a smart membrane with pores drilled to 10 nanometers in diameter—the size needed for nitrate ions to pass through.

supercomputers and led by physicist Bill Wilson, uses a numerical method for calculating the electrostatic field in the vicinity of the charged membrane pore surfaces. The modeling takes into account an ion's unique 3D geometry and electronic charge distribution. Its motion through the membrane is determined by potentials applied to the membrane elements. The modeling results determine the pore size and the optimum voltage to be applied to the membrane. "Water purification research has always been an empirical field," says Bourcier. "We're modeling the membranes before they are manufactured to avoid a lot of trial and error."

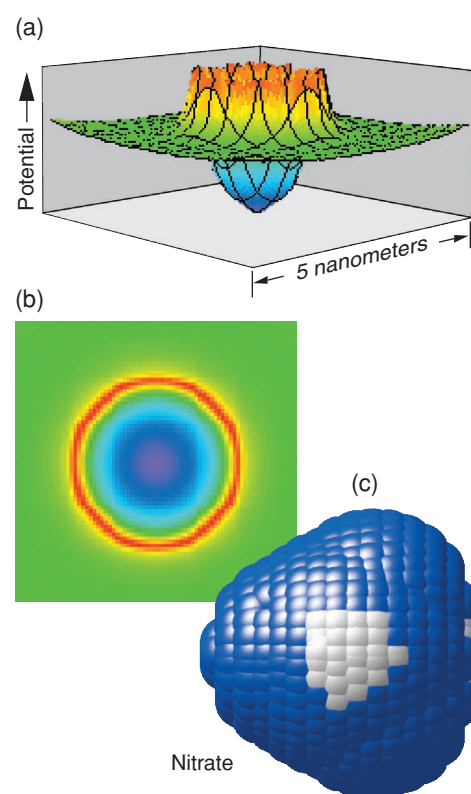
The project team also wants to research contaminants besides nitrate. Many community wells do not meet the new lower limits for arsenic, but treating them with reverse osmosis would cost millions of dollars. Electrodialysis with smart membranes could be a viable alternative. Other contaminants of interest include perchlorate, a by-product of rocket fuel that is found in Santa Clara County groundwater, and selenium, a natural element found in Central Valley groundwater and elsewhere.

Within a year, the researchers plan to test a prototype unit in the field, and they are evaluating potential demonstration sites. Bourcier believes that the technology will be capable of purifying a metric ton of water for 20 cents in energy costs, half of current costs. In addition, large-scale smart membrane manufacturing would cost less than a dollar per square meter.

The team is confident the pores also could be used to trap minor contaminants, such as perchlorate molecules, which typically are present in parts-per-billion concentrations. For those applications, the voltage applied to the membranes would be turned up to electrochemically destroy the perchlorate molecules and, thus, eliminate any waste stream.

In a similar manner, a membrane could be designed to selectively remove

viruses and then deactivate them. Bourcier foresees specialized membranes for the military, such as a unit mounted on a Humvee to purify brackish water for troops in the field, or membranes designed to remove chemical and biological warfare agents from water. The technology could also be used to purify the wastewater from the production of oil, gas, and coal and to recover metals in industrial wastewater and in silicon chip manufacturing. "There are



Quantum mechanical modeling is being used to design the smart membranes. (a) A simulation of a smart membrane pore shows the strong electric field gradients near the pore surface, where blue is the lowest voltage and red is the highest. The electrostatic forces will induce a nitrate molecule to pass through the pore where the molecule can be collected in a waste stream. (b) The same gradient is shown from the top, looking down on the pore. (c) This model shows the charge distribution of a nitrate ion, where the white area denotes an area of negative charge.

many tricks we can try,” says Bourcier. “If we’re successful, we’ll see much greater use of electro dialysis.”

California Again Leads the Nation

Newmark says she is seeing results from early progress of the Water Initiative. For example, Livermore researchers have received letters of endorsement from many water districts and agencies. “Successful development of these tools and methods may revolutionize the options water managers have to address the challenges facing them.”

Although the immediate focus is California, the Livermore tools and methods can be applied anywhere in the nation. The state, Newmark says, is akin to “a canary in a coal mine” because looking at California’s water picture is like looking at America’s water future.

—Arnie Heller

Key Words: denitrification, electrodialysis, global climate change, hydrologic cycle, Laboratory Directed Research and Development, nitrate contamination, water purification.

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